Hydrogen Generation From The Catalyst Decomposition Of Hydrazine

Project work

Submitted for partial fulfillment of the BSC degree in chemistry

By

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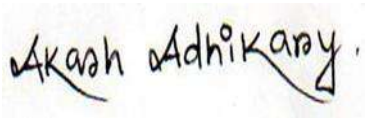

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Abstract:

The synthesis of highly active and selective catalysts is the central issue in the development of hydrous hydrazine (N2H4·H2O) as a viable hydrogen carrier. Herein, we report the synthesis of bimetallic Ni-Ir nanocatalyts supported on CeO2 using a one-pot coprecipitation method. A combination of XRD, HRTEM and XPS analyses indicate that the Ni-Ir/CeO2 catalyst is composed of tiny Ni-Ir alloy nanoparticles with an average size of around 4 nm and crystalline CeO2 matrix. The Ni-Ir/CeO2 catalyst exhibits high catalytic activity and excellent selectivity towards hydrogen generation from N2H4·H2O at mild temperatures. Furthermore, in contrast to previously reported Ni-Pt catalysts, the Ni-Ir/CeO2 catalyst shows an alleviated requirement on alkali promoter to achieve its optimal catalytic performance. Also bimetallic Ni60Pd40 nanocatalyst with large surface area exerts 100% selectivity towards hydrogen generation from hydrous hydrazine under alkaline and ambient reaction conditions.

Introduction:

100% conversion N2H4·H2O to H2 light state [17-19,25-29]. But nonetheless these advances, continue to Hydrogen storage is the main enabling technology for its propagation
of hydrogen as an energy carrier. Wide decades of study of interstitial metal hydrides, complex hydrides and high-specific-area physisorbent did not lead to any functional material conversely, it can store moderate amounts of hydrogen (> 6 wt%) temperature with fast kinetics [1,2]. Recently, enough effort has been directed towards the chemical hydrogen storage materials as an alternative solution for vehicles or portable H2-source applications [3,4]. Among the materials of interest are Hydrazine monohydrate (N2H4 · H2O) is a leading candidate for the chemical hydrogen storage applications. N2H4.H2O appears in liquid form at ambient temperature with high hydrogen concentration (8 wt%), comparatively low cost, and satisfactory stability under ambient conditions [5]. Importantly, unlike other chemical hydrides, N2H4·H2O does not yield no solid by-product in its decomposition reaction, which offers clear advantages of compact design of practical H2-source system.

$$N2H4 \rightarrow N2 + 2H2 \quad (1)$$

$$3N2H4 \rightarrow N2 + 4NH3 \quad (2)$$

Effective hydrogen storage component of hydrazine (N2H4), $N_2H_4 \cdot H2O$, which decomposes through the following two competitive pathways Eqs. (1) and (2). Development of N2H4.H2O as an effective hydrogen carriers requires advanced catalysts that can selectively promote hydrogen

generation (HG), and already control the generation of NH3 derived from N2H4.H2O. In addition, the H2 dilution effect by N2 on fuel cell performance needs to be carefully investigated and novel technology may be needed to separate H2 from the H2 / N2 mixture [2,3]. Over the past decade, several noble or non-noble metals and their alloys have been applied for N2H4 · H2O decomposition [8-30].It was found that Group VIII was a preferred choice in the transition metal, and its combination with noble metals (e.g. Pt, Ir, Rh) may result significant improvement on catalyst activity and response selection from N2H4 · H2O [12–15,18,19,22-29] to HG. In addition, it has

experimentally revealed that the use of basic aids stable catalyst nanoparticles can lead to improved stability and improved H2 selectivity [17-22,25-29]. Allowance's employment and stabilization techniques have given birth to a series of Ni-based alloy catalyst, which enables fast and almost be Ni-based alloy catalysts improved in terms of catalyst performance. For example, currently available Ni-based catalysts usually show poor durability, which severely limits their potential application to H2-source systems [17-19,21-24,27-29].Catalyst HG from N2H4 · H2O on Ni-based catalysts usually require the addition of alkali catalysts, which can be corrosion causes problems in equipment applications [11,16,21-29].In addition, Ni-based catalysts show that optimal catalysts properties are usually a large fraction of the noble metal, which greatly increase catalyst costs.

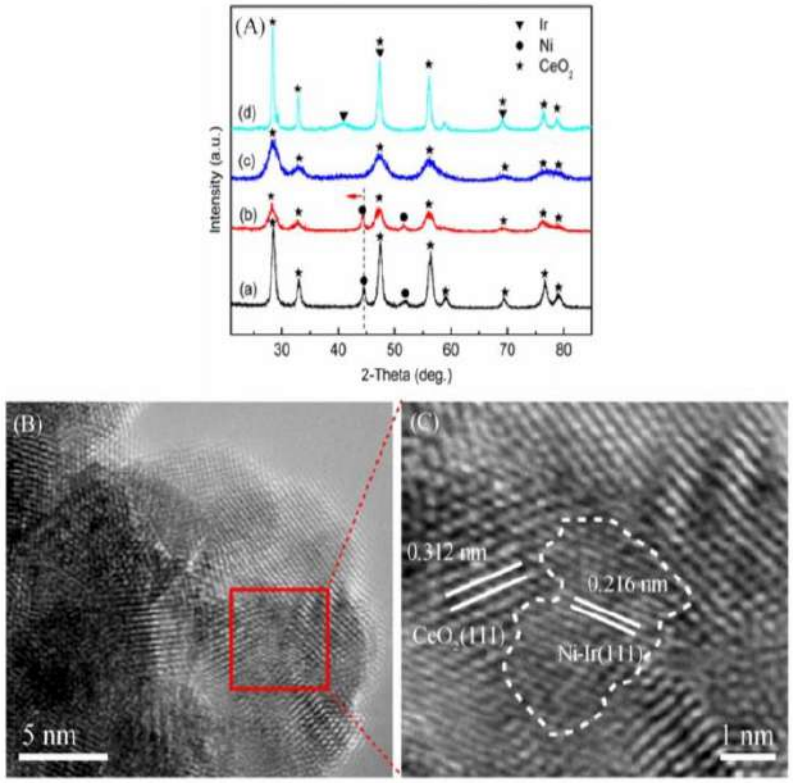


Fig. 1. (A) XRD patterns of (a) Ni/CeO_2, (b) $Ni_{91}Ir_9/CeO_2$, (c) Ir/CeO_2 catalyst samples and (d) the post-calcined Ir/CeO_2 catalyst at 750 °C; (B) HRTEM image of the $Ni_{91}Ir_9/CeO_2$ catalyst; (C) HRTEM image of the region indicated by the red rectangle in (B).

In our efforts to address the above issues, we have seen that include the small amount of Ir element in the Ni catalyst can dramatically improve catalytic properties from N2H4 · H2O to HG. The

optimized catalyst enables the complete conversion of N2H4 · H2O to H2 at moderate temperatures. Moreover, unlike previously reported the Ni-Pt catalyst shows the relief requirements of the Ni-Ir catalyst alkali promoters to achieve its optimal catalytic performance. We herein our preliminary report along with these experimental results understanding Ir-induced changes in catalytic responses.

we report a very simple room temperature method of preparing Ni-Pd nanocatalyst (Ni content is 60%) by a surfactant assisted co-reduction of hydroxides of Pd2+ and Ni2+ by hydrazine without using any support material, still contributing a very high surface area of 150 m2g-1, highest reported so far in this class of catalysts, with 100% selectivity towards hydrogen generation from hydrous hydrazine at room temperature where NaOH acts as promoter for complete hydrazine decomposition.

Experimental:

2.1 Chemical and catalytic preparations:

Nickel nitrate hexahydrate (Ni(NO3)3.6H2O, 98%), hexachloroiridium acid hexhydrate (H2IrCl6 · 6H2O, Ir content up to 35%), Cerium(III) Nitrate Hexahydrate (Ce(NO3)6 · 6H2O, 99%), Methanol (CH3OH,99%),sodium hydroxide (NaOH, 96%) and tetramethylammonium hydroxide (TMAH) was purchased from Aladdin. N2H4·H2O (99%) was purchased from Alfa Aesar. All reagents obtained are used. Deionized water was used throughout the experiment.

A series of Ni100-x-Irx / CeO2 catalysts with a specific metal / CeO2 molar ratio of 1: 1 was prepared by one-pot coprecipitation method, where x represents the molar part of Ir (Ni + Ir). In a general method of preparation, 5 mmol of Ce (NO3) 3 and 5 mmol of Ni (NO3)2 , H2IrCl6 mixture dissolved in 60 ml of CH3OH and the other 20 ml CH3OH solution containing 50 mmol TMAH dropwise added under magnetic excitation. After standing at 50 C for 1.5 h, the final solution was concentrated to separate the remaining black powder, which was cleaned with more deionized water. The cleaned powder was then vacuum is then dried at 120 C for 12 h. There were powder samples annealed at 500 ° C in air for 2 hours with a ramping rate of 2°cmin^-1 and H2 / Ar flowing for 1.5 hours decreases to 300 ° C under the atmosphere. All the as-ready catalyst sample was stored in an Ar-filled glove box to minimize oxidation.

2.2. Characterization of the catalyst:

Powder X-ray diffraction (XRD) data were obtained at Rigaku D /MAX-2500 VPC Diffractometer with Cu Kα radiation. X-ray photoileck- Tron spectroscopy (XPS) was performed on an ESCALAB 250 with Al Kα radiation High-Resolution Transmission Electron Microscopy (HRTEM)measurements were performed on a FEI Tecnai F30, which was equipped with an energy scattering X-ray spectroscopy (EDS) analysis unit catalyst is conducted a component analysis of the sample inductively combined plasma-atomic emission spectrometry (ICP-AES, Iris intripid).

2.3. Catalyst activity evaluation

Catalytic decomposition of N2H4 H2O was performed a 50 ml two-neck round flask. At the time of measurement, the flask was Placed in a thermostat, which was equipped with a water conductor the system for maintaining the reaction temperature. In a general measureshipment, alkaline aqueous solution containing powder catalyst was before- heated to a certain temperature, and then N2H4 · H2O is injected in the solution to start the decomposition reaction. Gaseous product is passed through a trap containing 1.0 M HCl for absorption NH3, if any, and then measured by a gravity water-displacement method.Weight data was automatically recorded by data acquisition software (one data every 10 seconds) and scheduled gas normalized to standard conditions. Gaseous products decomposition was analyzed by gas chromatograph from N2H4 · H2O (GC, Agilent 7820 A), which was equipped with a molecular sieve 1 3X column and a thermal conductivity detector.

In determining the response rate (h-1)all metals were atoms estimation of catalyst response and required time participation N2H4 was used in the calculation for 50% conversion of H2O. The selectivity from N2H4 · H2O (X) to HG was calculated as follow Eq. (3), which can be taken from Eqs. (1) and (2).

X=3Y-1/8[Y=n(N2)+n(H2)/n(N2H4)]. (3)

2.4 Synthesis of NixPd100-x BMNPs

NixPd100 x (x ¼ 50e90) was co-synthesized by BMNPs decrease in hydroxide of Pd^{2}+ and Ni^{2}+ in the presence of PVP 298 K of PdCl2. 0.0297e0.1191 g (depending on atomic ratio Pd of NixPd100-x was dissolved in 20 mL of 0.1 M HCl solution and stir for 30 minutes. 0.3594e0.2396 g of NiCl2 has been added and stir for another 30 minutes. The resulting mixture was then dropwise was added with 10 ml constant stir of 1 M NaOH solution containing 0.0089 g PVP. Finally, 1 ml of 100% hydrogen hydrate solution was added to it; Instantly black NPs are formed. The NPs were separated, washed with several deionized water and dried at room temperature. Pd and Ni NPs was synthesized by a similar method for comparison.

Results and discussion:

In this work, we have prepared a series of monometallic Ni, Ir and Ni-Ir supported in CeO2 using bimetallic nanocatalyst one-spot caprices petition procedure. Here, CeO2 is selected as the support material based on its strong originality and high stability in alkaline reactions status Figure 1A represents Ni / CeO2, Ir / CeO2 and its XRD pattern and a representative Ni-Ir / CeO2 catalyst sample. Its evolution peaks, fluorite phase CeO2 (JCPDS No. 43-1002) was clearly observed all catalytic specimens indicate the crystal nature of the series. Comparison with Ni / CeO2 catalyst, contains the Ir catalytic sample showed a significantly weaker peak of CeO2, The inclusion of Ir in the catalyst suggests that may be annoying Crystal growth of CeO2 nanocrystallite. Significantly, the peak of evolution Ni-Ir / CeO2 metallic Ni was detectable in bimetallic catalysts, however The simultaneous Ir included in the XRD analysis was invisible Ni-Ir grain size of Ni91Ir9 / CeO2, based on Scherrer equation the catalyst was calculated as ~ 4.3 nm. XRD is a close test Patterns found that Ni (111) peaks of Ni-Ir / CeO2 catalysts have shifted Slightly towards a lower angle, compared to its characteristic peak Fcc Ni in the Ni / CeO2 catalyst. These results are clearly recommended substitution of large Ir atoms for smaller Ni atoms, resulting Ni-Ir solid-soluble alloy formation. There was more to this speculation. Supported by HRTEM monitoring of representative Ni-Ir / CeO2 catalyst sampling. Seen as figs. 1B and C, catalysts mainly Made up of two types of tiny nanocrystallites, including random orientation, which is consistent with XRD results. Nanocrystallites With a mesh fringe distance of 0.216 nm, which is within the values (111) plane of fcc Ni (0.203 nm) and plane (111) of fcc Ir (0.222 nm), can be safely assigned to the Ni-IR alloy. Measured lattice. The marginal distance coincides well

with the (111) plane of 0.312 nm CeO2. In addition, HRTEM images clearly show scattering Ni-IR nanoparticles with an average size of about 4 nm in CeO2 matrix, which corresponds to XRD results.

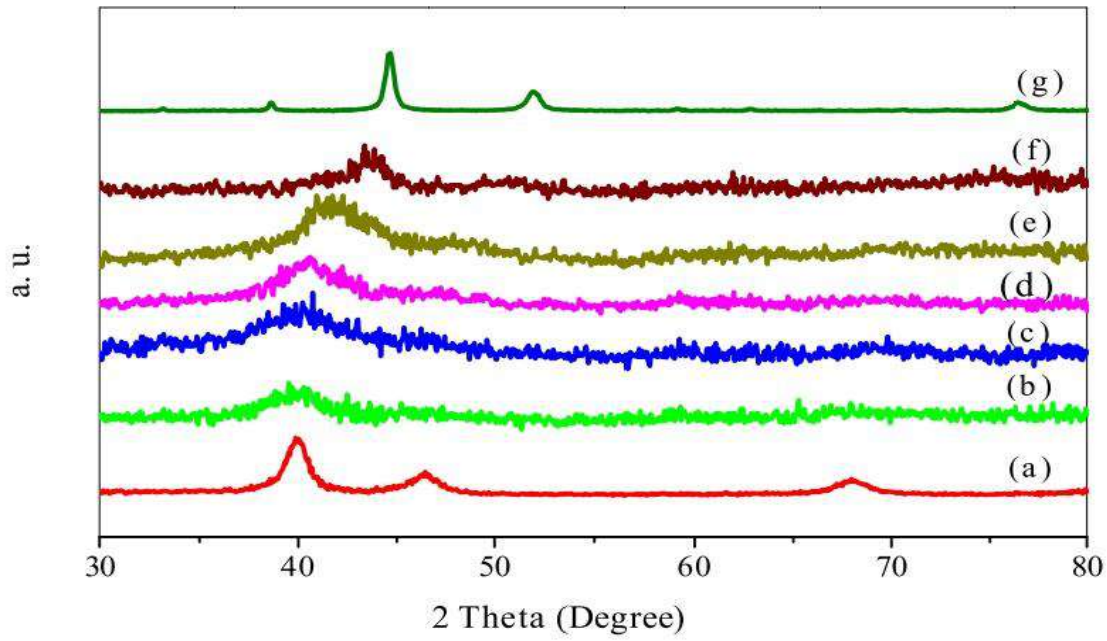


Fig:-1.1 XRD patterns of the (a)Pd, (b)Ni50Pd50, (c)Ni60Pd40, (d)Ni70Pd30, (e)Ni80Pd20, (f)Ni90Pd10, (g)Ni NPs

XRD profile of Pd, Ni and NixPd100 x (x ¼ 50e90) NPs (Figure 1.1) synthesized face expression under similar experimental conditions concentrated cubic (fcc) pattern of the prepared nanocatalyst. XRD the pattern of the prepared Pd and Ni NPs (Figures 1a and g) is correct match the literature reporting standards (JCPDS, 1995, file no.Indicates the structure of 05-0681 for Pd and 65-0380 for Ni) phase pure Pd and Ni NPs only. NixPd100 x NPs shows only one (111) visible prominent scattering peaks related to the plane palladium's it is observed that with increasing Ni content the scattering peaks of Ni50Pd50, Ni60Pd40, Ni70Pd30, Ni80Pd20, Ni90Pd10 move to higher angles than Pd NPs. In the absence the XRD of the NixPd100 x NPs features pure Pd and Ni peaks .(Figure 1.1b-f) indicates that the prepared NixPd100 consists of x NPs of bimetallic phase instead of monometallic physical mixture Pd and Ni NPs. XRD pattern of Sine's physical mixture the Ni and Pd (1: 1 mol ratio) consist of separate peaks related to pure Ni and Pd NPs. As the Ni / Pd ratio increases, Word suggests higher angles this changes the interplanetary interval of NixPd100 x BMNPs combination of feed molar ratio of Ni to Pd. As expected, the trend indicator that follows the lattice parameters shift formation where lattice contraction occurred with a increase in nickel content due to replacement of small nickel atoms for large palladium atoms [22-24]. NixPd100 x Bimetallic the elongated structure can be explained by the Humerotheri rule [25,26], which says that when the relative difference of the atomic radii.

To gain insight into the chemical state and the electronic state material material, we conducted a comparative XPS analysis Ni-Ir / CeO2, Ni / CeO2 and Ir / CeO2 catalyst samples (no results Shown). It has been found that both Ni and Ir look chemically various entities related to metallic and oxide conditions, and the latter should be primarily responsible for surface oxidation catalyst sampling. In comparison with relevant monometallic catalyst, Ni-Ir / CeO2 bimetallic catalyst showed no admiration the material changes in terms of the binding strength of the material, whichindicates the lack of charge transfer between the Ni and Ir elements.

Catalyst performance of Ni-Ir / CeO2 catalyst series towards digestion of N2H4 H2O has been tested and compared relevant monometallic catalysts. As shown in Figure 2, Ni / CeO2 the catalyst shows a high H2 selectivity (96%) and a low response rate(14.2 h-1).But when a small amount of Ir elements were included Ni-Ir forms alloys in Ni, resulting in Ni-Ir / CeO2 catalyst significantly increased catalytic activity and improved H2 selectivity. For example, the Ni19Ir1 / CeO2 catalyst showed a more than 2-fold increase catalyst activity. Ir increases the fraction further, Ni91Ir9 / CeO2 catalysts have shown the best catalyst performance. It is fully active N2H4 · H2O to H2 decomposes in the presence of 0.5 M NaOH at a temperature of 50 ° C,with an average response rate of 97 h-1. Figure 3 presents the GC results gas mixture from Ni91Ir9 / N2H4 · H2O decomposition over the Ni91Ir9/Ceo2 catalyst.

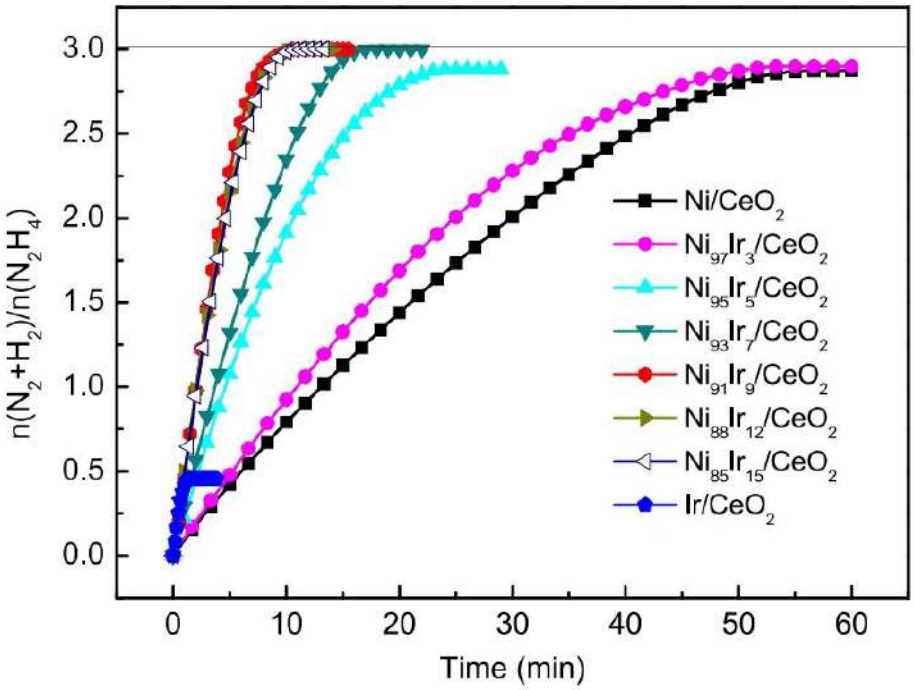
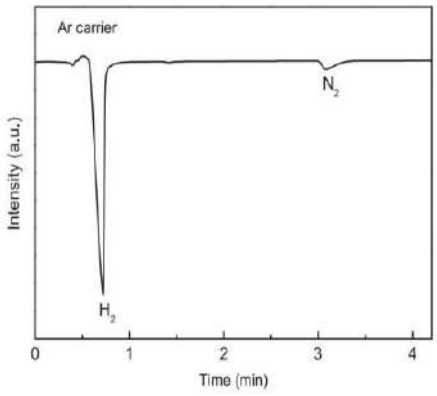


Fig. 2. Time course profiles of the system composed of 4 mL of 0.5 M $N_2H_4 \cdot H_2O$+0.5 M NaOH aqueous solution and the $Ni_{100-x}Ir_x/CeO_2$ catalyst at 50 °C. The catalyst/$N_2H_4 \cdot H_2O$ molar ratio was fixed at 1:10.

Understand the process of change of Ir element better catalyst response is clearly significant for developing behavior high-performance N2H4 · H2O decomposition catalyst. The theoretical and experimental studies have shown that Ni and Ir are different sufficient from each other in terms of absorption properties and catalytic reaction pathways of N2H4 molecules [8,17,19,31,32]. The N2H4 molecule absorbed in Ir (111) prefers a bridging configuration the bond of Ir atom with both N atoms and its N-N axis is parallel Ir surface. Since N2H4 has a lot of N-N bond strength (2.60 eV) less than the N-H bond (3.60 eV),N2H4 is easily expected N-N bonds dissociate through cleavage to form amide radicals which then react with other N2H4 molecules to yield Nh3 and N2 [31].



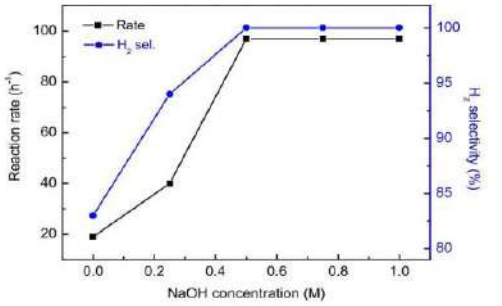


Fig. 4. Effect of NaOH concentration on reaction rate and H_2 selectivity of the system composed of 4 mL of 0.5 M $N_2H_4{\cdot}H_2O$+x M NaOH aqueous solution and the $Ni_{91}Ir_9/CeO_2$ catalyst at 50 °C. The catalyst/$N_2H_4{\cdot}H_2O$ molar ratio was fixed at 1:10.

Fig:3. GC result of the gaseous mixture from

N2H4.H2O decomposition over the Ni91Ir9/CeO2 Catalyst

Alkali is an effective promoter for the catalytic HG from N2H4·H2O, and its concentration exerts considerable influence on the reaction rate and H2 selectivity [11,16,21–29]. Typically, high concentration of alkali promoter is required for obtaining favorable HG performance from catalytic decomposition of N2H4·H2O. For example, the Ni-based catalysts, like Ni-Mo-B/La(OH)3 [21], Ni-Pt/CeO2 [25], and Ni-Pt/La2O3 [28], were reported to exhibit their optimal catalytic performance in the presence of 1∼3 M NaOH. In the present study, we found that the Ni-Ir/CeO2 catalyst required a much lower NaOH concentration of 0.5 M to exert its optimal catalytic performance, as seen in Fig.4 Since concentrated alkaline solution may cause corrosion problem in the practical apparatus application, an alleviated requirement of alkali promoter im+plies an important advantage of Ni-Ir/CeO2 catalyst over the previously reported Ni-based catalysts.The catalytic decomposition behavior of N2H4·H2O over the Ni91Ir9/CeO2 catalyst was further examined at varied temperatures. As seen in Fig. 5, the decomposition rate of N2H4·H2O increases with increasing reaction temperature. For example, increasing reaction temperature from 30 to 70 °C results in an over 20 times increase of the decomposition rate. Intriguingly, the increase of decomposition rate was not accompanied with the

change of reaction selectivity. The catalytic decomposition of N2H4·H2O over the Ni91Ir9/CeO2 catalyst exhibited 100% selectivity to HG at the examined temperature range from 30 to 80 °C. Since the decomposition reaction of N2H4·H2O is exothermic, high and temperature-independent H2 selectivity of the catalyst is clearly a desirable attribute for practical applications.

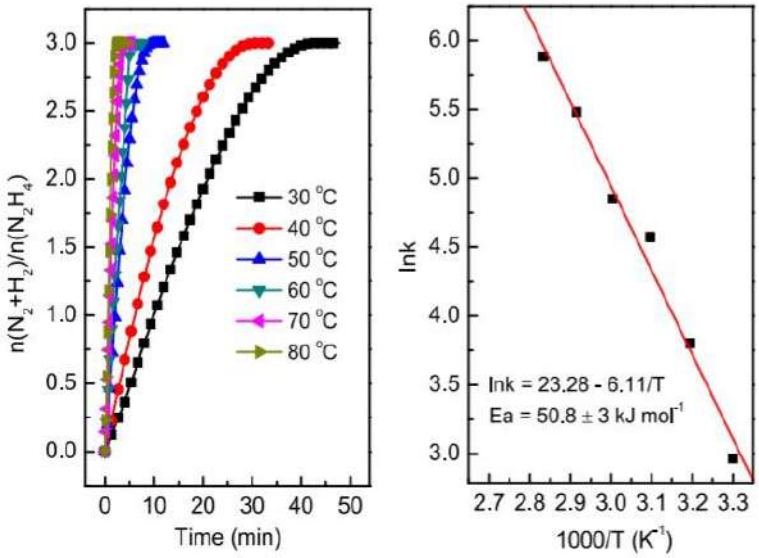


Fig. 5. (Left) Decomposition kinetics curves of the system composed of 4 mL of 0.5 M N_2H_4·H_2O+0.5 M NaOH solution and $Ni_{91}Ir_9/CeO_2$ catalyst at varied temperatures; (Right) Arrhenius treatment of the temperature- dependent rate data for determination of the apparent activation energy.

Finally, the Ni91Ir9/CeO2 catalyst was subjected to cyclic usage in the N2H4·H2O solution to test its durability. As seen in Fig. 6, the catalyst retained 100% H2 selectivity even at its 15th time usage, but the catalytic activity gradually decreased with increasing the cycle number.

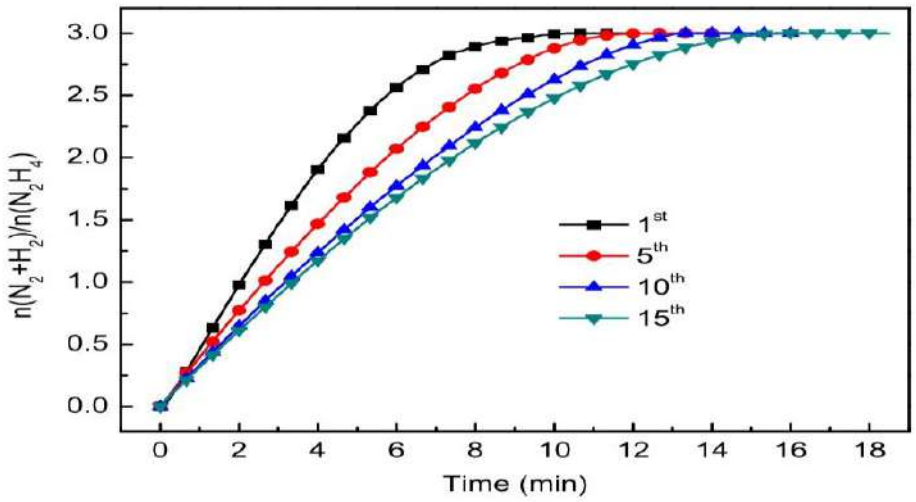


Fig. 6. Cyclic performance of the $Ni_{91}Ir_9/CeO_2$ catalyst in catalyzing the decomposition of N_2H_4·H_2O in the presence of 0.5 M NaOH at 50 °C.

After 15 cycles of reaction, the reaction rate decreased to 58.4 h-1, corresponding to ~60% of the initial level. Similar activity degradation was repeatedly observed in other Ni-based catalysts [17–19,21-24,27,28].

Conclusion:

In summary, we report a highly active bimetallic Ni60Ir40 nanocatalyst made by a soft chemical method which exhibits 100% hydrogen selectivity for complete decomposition of hydrous hydrazine ,as the Ni-Ir/CeO2 Catalyst not only exhibit excellent catalytic activity and high selectivity towards hydrogen generation from N2H4.H2O,but showed an alleviated requirement of alkali promoter. The improved catalytic performance is primarily contributed to the formation of Ni-Ir alloy. Better understanding of the Ir-induced modification of electronic structure is clearly of significance for the rational design of N2H4·H2O decomposition catalysts**.**

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RECENT PROGRESS ON THE FIELD OF FLUORESCENT CHEMOSENSORS

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of ***Dr. Debabrata Jana***

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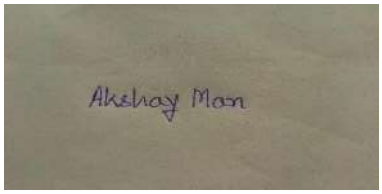

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RECENT PROGRESS ON THE FIELD OF FLUORESCENT CHEMOSENSORS

ABSTRACT

Fluorescent chemosensors have been widely applied in many diverse fields such as biology, physiology, pharmacology, and environmental sciences for the detection of biologically and/or environmentally important species. The field of fluorescent chemosensors is being developed for about 150 years. Since then a wide range of chemosensors had been discovered. Despite the progress made in this field, several problems and challenges still exist. This review article provides a general overview of the development in the research of fluorescent sensors. The application of chemosensors in various established and emerging biotechnologies is very bright.

Keywords: Supramolecular Chemistry, Biosensors, Chemosensors, Bioimaging.

INTRODUCTION

Chemosensors are molecular structures that are used for sensing an analyte. When it binds with a specific ion or molecule it produces an observable change that signals the presence of that particular ion or molecule. Fluorescent chemosensors are consisted with a fluorophore part and a binding site. If the binding sites operate via irreversible chemical reactions then the indicators are described as fluorescent chemodosimeters.

The first fluorescent chemosensor was reported by F. Goppelsro¨der in 1867. It was used for the determination of aluminum ion (Al^{3+}) through the formation of a strongly fluorescent morin chelate. Since then a number of fluorescent chemosensors have been developed for the determination of many other metal ions. In this short review we are going to present the subsequent development of chemosensors and their uses in various biological and analytical processes.

At the very beginning, chemosensors were used to detect only metal cation rather than anions and neutral species. This is because these compounds can easily bind metal ions in water. Around 1980, de Silva and Czarnik who are regarded as two fathers of modern

chemosensors, pioneered the growth in the development of fluorescent chemosensors. Since those pioneering days, an extensive development of fluorescent chemosensors as well as the scope of their applicability in numerous biological fields, have been extended.

National status: In the last decade huge development has been done by the Indian scientist in the field of chemosensors. Detection of toxic metal ions or bio-molecules is one of the most challenging research fields today. Prof. K. Ghosh and his co-workers designed and synthesized new type of chemosensors for sensing of cations, anions, neutral molecules. Prof. Moorthy and co-workers have significant contribution in the field of supramolecular chemistry and published huge number of research work in the international journel. Prof. Ramanathan and his co-workers performed various research works on the development of fluorescence probes for binding specifically different biological molecules. Prof. N. Parveen and co-workers also carried out evolutionary work in the field of fluorescence imaging using water soluble small molecules. Prof. Chowdhury and his co-workers have significant contribution in the field of Single fluorescence Sensor in solid state using polymer–thin film. The dignified work on the field of fluorescence sensing of biophysically relevant analysis has been improved by of Prof. A. Dutta and his co-workers. Prof. R. Anand and co-workers have also sincere work in the field of biosensors for detecting organic pollutants and process for producing the same. Prof. T. Majumdar and his co-workers have done extensive research work on the field spectroscopic and computational studies of some optical sensors of metal ion and anion. Prof. A. K. Mahapatra and his co-workers carried out versatile research work on the field of Chemosensors, Chemodosimeter and Supramolecular chemistry. This group developed novel small molecules for sensing of metals ions in solution phase.

DISCUSSION

Fluorescent chemosensors for cations: Human body and the environment contains large number of metal ions among them some are essential for our life such as sodium (Na^+) potassium (K^+), calcium (Ca^{2+}), copper (Cu^+ and Cu^{2+}) and zinc (Zn^{2+}) and some are toxic and hazardous such as lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}). To detect these metal ions selectively, a number of chemosensors have been developed.

Fluorescent chemosensors for alkali and alkaline earth metal ions: The mechanism of binding of metals by fluorescent chemosensors involves coordination interactions between the hosts and the guest .Two naphthalene based chemosensors are shown in (Fig 1) i.e. **1** and **2** which

also exhibit dichotomous behaviour. It was observed that when 1 formed a complex with alkali metal chloride salts in 95% ethanol glass at 77 K it displayed a decrease in fluorescence quantum yield, also an increase in phosphorescence quantum yield, and a slight decrease in phosphorescence lifetime but for the complexation of **2** with potassium (K^+), rubidium (Rb^+), or caesium (Cs^+) chloride salts caused a noticeable increase in fluorescence quantum yield, also a decrease in phosphorescence quantum yield, and a substantial decrease in phosphorescence lifetime. The reason behind these changes are the heavy atom effect (for Rb^+ and Cs^+), complexation induced change in triplet energy relative to the ground and excited singlet state energies as well as rigidification and conformational effects.

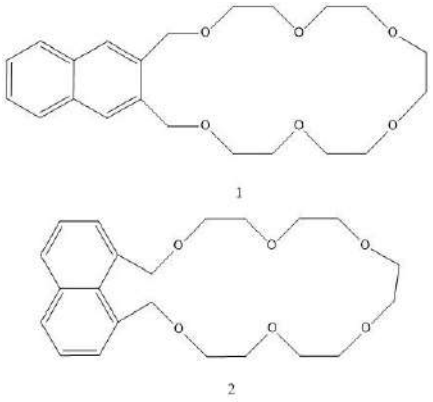

Fig.1: Structures of the fluorescent chemosensors **1, 2**.

Fluorescent chemosensors for d-block metal ions:

The uses of chemosensors is not only limited for the detection of alkali metal and alkaline earth metal ions but also they are used to capture the transition metals since these metals take part in various chemical reactions.

Copper (Cu), the third most abundant transition metal in the human body, is involved in various physiological and pathological processes. Imbalance of copper causes diseases like Menkes (copper deficiency), Wilson's (copper overload), Alzheimer's disease, prion disorders, neurodegeneration and cancer.

In 1997, Czarnik and co-workers developed a rhodamine-B derivative and its ring-opening reaction for sensing copper ion (Cu^{2+}).

Fluorescent chemosensors for anions:

Anions play an important role in biological and industrial processes also the environment contains a number of anionic pollutants. There are a number of fluorescent chemosensors

have been developed for the detection of anions have used host–guest interactions or chemical reactions, over the past several decades. The mechanism through which they bind with ions may be a guest host interaction or may be a chemical reaction.

Fluorescent chemosensors for small neutral molecules:

We have various neutral molecules in environment .While small neutral molecules such as reactive sulfur species (RSS) and some neutral ROS/RNS are essential for our survival, some small neutral molecules like nitroaromatics (explosives), and nerve-gas are a threat to health. These two important reasons have stimulated the development of fluorescent chemosensors for small neutral molecules over recent years.

Fluorescent chemosensors for reactive sulfur species (RSS): Intracellular thiols such as cysteine (Cys), homocysteine (Hcy) and glutathione (GSH) have vital roles in biological systems. Abnormal levels of these molecules can cause a number of diseases, such as liver damage, leucocyte loss, psoriasis, cancer and AIDS. That is why the detection of these thiolcontaining biomolecules in biological samples has become very important. The first use of PET sensors for thiols was demonstrated by de Silva in 1998. In 2004, two squaraine based fluorescent chemosensors 33a and 33b (Fig.2) was developed for the detection of thiols by Martı´nez-Ma´n˜ez and co-workers. Due to the selective addition of thiols to the cyclobutene ring in the chemosensors these solutions showed colour changes from blue to colorless in the presence of thiol-containing compounds. These thiol chemosensors cannot distinguish Cys/Hcy and GSH.

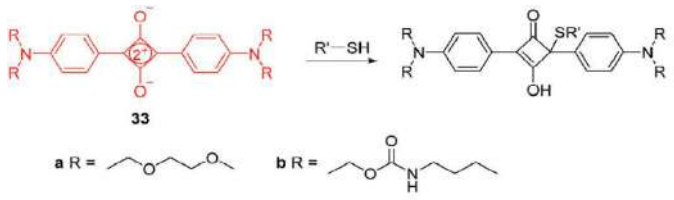

Fig. 2: Structures and proposed mechanism of **33 (a)** and **(b)** for detection of thiols.

Fluorescent chemosensors for biomacromolecules:

In living biological systems biomacromolecules play a vital role. However, the abnormal function of these biomacromolecules often has huge impact on living bodies. The fluorescence imaging techniques is a powerful tool for studying these biomacromolecules and to fully understand their purpose in these complex biological systems. The chemosensors

show excellent spatial and temporal resolution and high molecular specificity with these biomolecules. The detection of biomacromolecules is not an easy task as they often have large molecular weights, complex structures and a range of biological functions. Over the past several decades, a number of fluorescent chemosensors have been developed, which have proven to be a must for bioimaging and used in the investigation of diseases.

Czarnik carried out pioneering work on anthrylpolyamine based chemosensors to sense polyanions such as heparin, poly-L-glutamate, ds DNA (double-stranded DNA) and ss DNA (single-stranded DNA) in water. These chemosensors display a redshift and a decrease in their emission spectra when they bound to either ds DNA or to ss DNA.

A pyrene-based peptide beacon (fluorescent chemosensor 46) has been reported by Schmuck and co-workers. It was shown to intercalate with DNA (Fig.3). While the folded conformation of 46 exhibits a typical pyrene excimer emission in solution, it undergoes a conformational change to the unfolded form when bound to DNA. During the change in conformation, a ratiometric change in fluorescence from excimer (490 nm) to monomer emission (406 nm) is observed.

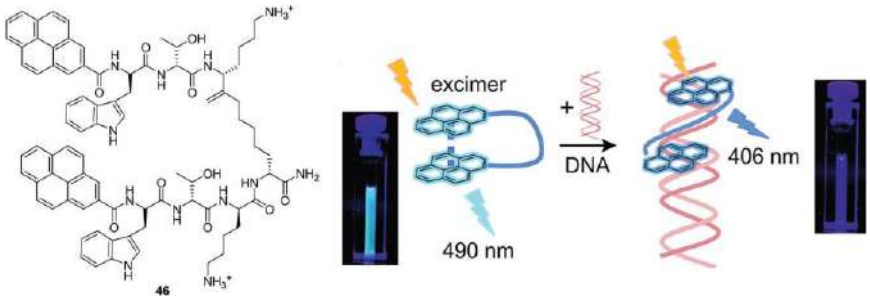

Fig.3: Structures of the fluorescent chemosensors **46** and the schematic illustration of **46** and Its Interaction with nucleic acid (the photographs show the corresponding cuvettes under UV light).

CONCLUSION

Over the past 50 years the field of fluorescent chemosensors has been developed explosively. The growth in this vast field is deeply pioneered by the research of Professor Anthony W. Czarnik's and Professor A. Prasanna de Silva. Within a very short time the field is flourished and is recognised as a branch of chemistry. Research workers expect that the field of chemosensors will continue to expand. To meet new challenges we need increasing number

of new and improved chemosensors as well as we have to find new approaches or applications of existing fluorophores.

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Palladium Catalysts Supported on Zeolite: A Review of the Recent Developments in the Heck-Mizoroki Coupling Reactions

Project Work

Submitted for Partial Fulfillment of the B.Sc. Degree in Chemistry

By

Atrajo Nandy

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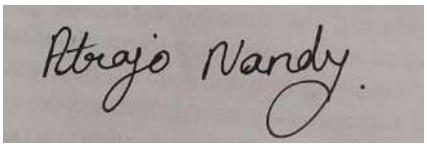

CERTIFICATE

Date: 27.01.2022

This is to certify that the project work entitled "Palladium Catalysts Supported on Zeolite: A Review of the Recent Developments in the Heck-Mizoroki Coupling Reactions" submitted by **Mr. Atrajo Nandy** (Registration No. A01-1112-112-005-2019) for the partial fulfilment of the B. Sc degree in Chemistry at Ramakrishna Mission Vivekananda Centenary College, Rahara has been executed under my supervision.

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Palladium Catalysts Supported on Zeolite: A Review of the Recent Developments in the Heck-Mizoroki Coupling Reactions

Atrajo Nandy

Abstract Over the last couple of decades, Pd-catalysed C-C bond forming reactions and generation of hydrogen from Pd-nanoparticles from organic compounds have gained immense interest and importance too for their applications in preparation of various biological and pharmaceutical fragments as well as for regeneration of cleaner and renewable sources of fuel such as hydrogen. Heterogeneous Pd-catalysts supported on porous materials, like zeolites, have a lot of advantages such as a high surface area, with changeable acidity and basicity, hydrophobic and hydrophilic nature, shape and size selectivity, as well as chemical and thermal stability. They can also be recovered, reused and regenerated very easily. This review covers the articles published on the various reactions which are supported by Pd-catalysts, and also their applications to an extent.

Keywords Palladium; Heterogeneous catalysis; Supported Catalysis; Zeolites; Coupling reactions; Nanoparticles

Introduction

Since, in the past few decades, a new era for construction of C-C bonds has come into light considerably, which has increased the ability of chemists to assemble complex molecular frameworks for many important applications. Also, the recent trend in development of various sources of economical and renewable fuels have led chemists to investigate the usage of heterogenous catalysts in the easy production of such fuels from various sources. The transition metal catalysts have the ability to create C-C bonds selectively within sensitive as

well as in the presence of various functional groups and that too under mild reaction conditions. Such reactions have opened up a gateway to new opportunities, particularly in the synthesis of medicinally and biologically important compounds [1]. Some of the commonly known Pd-coupling cross reactions are Mizoroki-Heck Reaction [2] , Suzuki-Miyaura [3], Negishi [4], Stille [5] reactions which have unparalleled importance in the synthesis of olefins, biphenyls, ketones and acetylenes. They are so significant that the Nobel Prize in Chemistry in 2010 was awarded to Professors Heck, Negishi and Suzuki for their magnificent work in this aspect. However, the separation of the catalyst from the reaction mixture is yet to be developed well and thus poses a challenge for the sustainable development of the reactions. The improved and efficient processes that are viable both economically as well as environmentally can be achieved partly by immobilization of Pd on suitable solid supports [6-11].

For the last 20 years, porous materials, particularly zeolites have been the centre of great interest due to their variable and controllable pH levels along with their hydrophobic and hydrophilicity, shape and size, as well as chemical and thermal stabilities. These properties offer them a wide variety of applications in the field of chemistry [12]. A wide variety of innovative strategies have been developed for generating zeolites containing transition metal catalysts [13]. Zeolites are crystalline aluminosilicates comprising of infinitely extending three-dimensional arrangements of SiO_4 and AlO_4 tetrahedra, connected via corner shared oxygen atoms. These tetrahedral units are referred to as primary building units, which are assembled into secondary building units, which are then assembled to form the three-dimensional framework structures containing channels and cages of discreet size.

Zeolites are sub-divided into three categories according to the number of O or Al/Si atoms that are present in the largest micropore apertures or according to the diameter of their pores (Ø):

1. Small-pore zeolites: these possess eight membered oxygen ring systems with free diameters of Ø 0.3-0.45nm. Examples of this type are zeolite A, chabazite and erionite.

2. Medium pore zeolites: these possess ten-membered oxygen ring systems with free diameters of Ø 0.45-0.60nm like ZSM-5 and ferrierite.

3. (a) Large-pore zeolites: these contain12-membered oxygen ring systems with free diameter Ø 0.60-0.80nm such as modernite, ZSM-12.

(b) Extra-Large pore zeolites: these contain 14-membered oxygen ring systems with free diameters of Ø 0.8-1.0nm.

Zeolites are technologically important minerals having a wide variety of applications including catalysis [14], ion-exchange [15], back-fill material for nuclear waste disposal [16] and chemical sensing [17]. Commercial applications include ion-exchange and catalysis. Its widest use is in the field of catalysis and is still increasing continuously. They can be used for Pd-catalysts because the mesoporous structure allow the diffusion of aryl substances selectively. They are moreover reusable without leaching or agglomeration of Pd. By changing and modifying the structure of zeolites, their catalytic properties can be enhanced. There are different ways to achieve this including direct hydrothermal synthesis and post-synthetic methods.

Pd supported on zeolites has many advantages. Some of them are:

i) the micropores and mesopores present help in encapsulating the Pd-species.

ii) the Al sites in the zeolites engender negative charges in the framework structure which provides zeolites and excellent ion-exchange capacity with Pd ion-exchange capacity with Pd^{2+} cations.

iii) The immobilized Pd complexes have the same or even considerably higher activity than their homogeneous counterparts as the zeolite framework probably better stabilizes the active Pd species.

iv) Zeolites are capable of stabilizing intermediate active species retained in their cavities due to their shape-selectivity.

v) The specific activity of Pd depends on the pH of the zeolite, hence making it possible to fine-tune the specific activity of the catalyst by tuning these properties by changing metal-support interactions.

In this review, the recent advances of Pd supported on different zeolites over the past few years in organic synthesis. In the beginning, we shall discuss the importance of cross-coupling reactions, and significance of zeolites as a support material for Pd catalysis. Next, we shall look at the various reactions and their applications for industrial as well as laboratory purposes. Also, we shall be discussing some methods by which renewable and

economical sources of energy can be generated. Finally, we shall summarize the significance of zeolite and Pd-zeolite catalysts and perspectives for further developments.

2 Reactions Involving Applications of Pd Entrapped in Zeolites

As zeolites have large specific surface area containing micropores and mesopores, they can be used for encapsulating of the Pd-complexes. The encapsulation minimizes the leaching of the Pd species into the solvent, which is a general problem associated with other Pd-supported catalysts. In addition, it also clears the problem of Pd agglomeration, as that leads to the deactivation of the catalyst due to the formation of Pd-black.

A) Mizoroki – Heck Coupling Reaction:

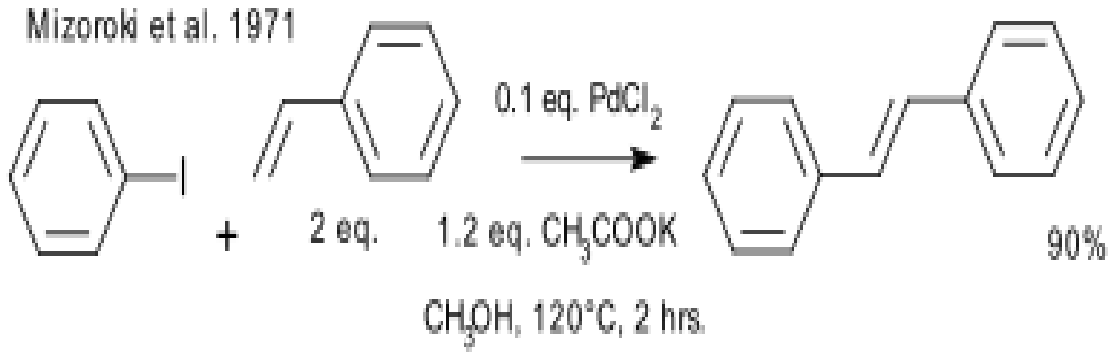
Since it was discovered [18], the Mizoroki-Heck reaction has become an excellent catalytic tool for new C-C bonds. This reaction is very efficient, enough to tolerate different functional groups with high selectivity [19]. Considering the importance of this reaction in organic synthesis and efforts to minimize the harsh reaction conditions, the first application of Pd-supported zeolite catalyst for Mizoroki-Heck reaction was reported by Dijakovitch et-al. It involves the formation of encapsulated complexes of Pd viz. $[Pd(NH_3)_4]^{2+}$, $Pd(OAc)_2$, $[Pd(C_3H_5)Cl]_2$ and $Pd[P(o\text{-}PhCH_3)_2(PhCH_2)]$ into the supercages of the NaY zeolite [20].

The Heck Reaction involves the reaction of an unstaturated halide (or triflate) with an alkene in the presence of a base and a Pd-catalyst (or Pd-nanometal based catalyst) to form a substituted alkene. It was one of the first reactions to follow the Pd(0)/Pd(II) catalytic cycle, the same cycle which was observed in other Pd(0)- catalyzed cross-coupling reactions. It is a very useful and efficient way to synthesize substituted alkenes.

[38]

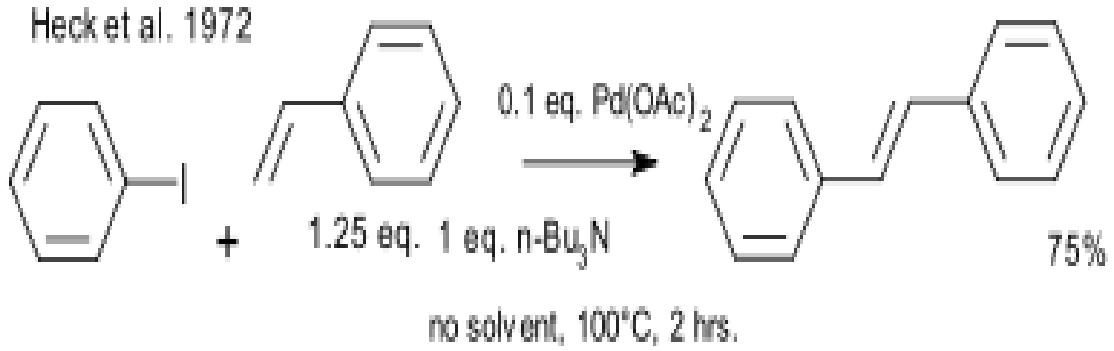
It originally describes the coupling between iodobenzene and styrene in methanol from stilbene at 120°C(autoclave) with potassium acetate base and $PdCl_2$ catalysis. This was an extension of an earlier work by Fujiwara on the Pd(II)-mediated coupling of arenes (Ar-H)

and alkenes [21].



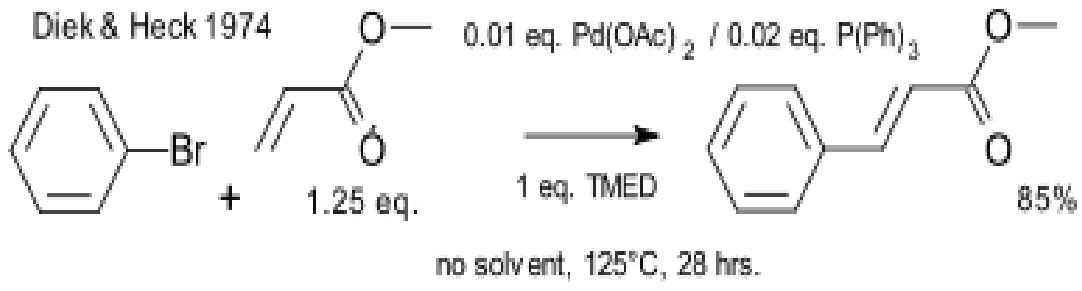
[38]

Heck, in 1972, acknowledged the Mizoroki publication. The reactions conditions differ in catalyst used [$Pd(OAc)_2$] was used here and catalyst loading [0.01eq], base used [a hindered amine] and lack of solvent [22][23].



[38]

In 1974, Heck introduced phosphine ligands into the equation [24].

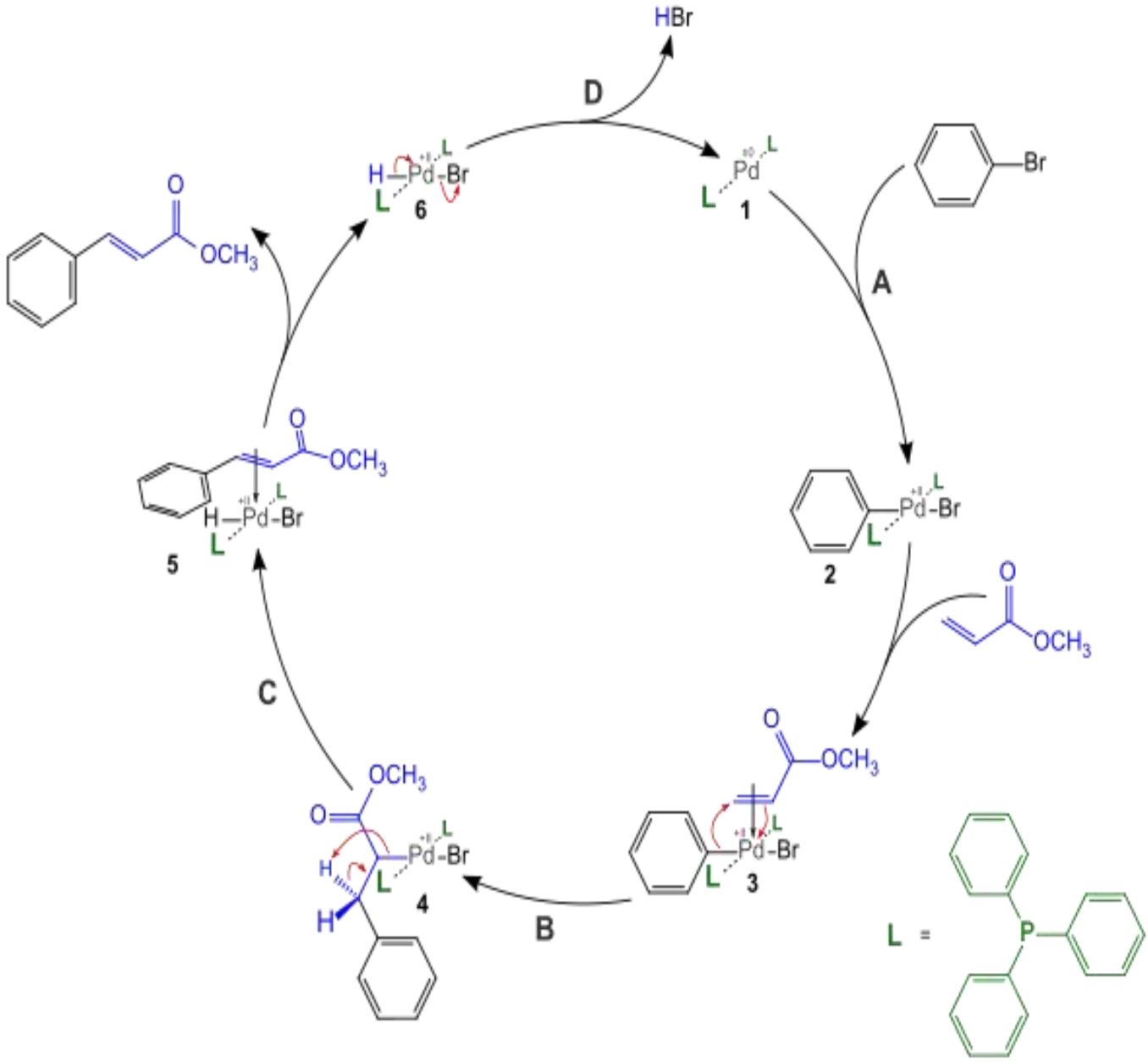


[38]

The aryl electrophile can be a halide (Br, Cl) or a triflate as well as benzyl or vinyl halides. The alkene must contain at least one sp^2 – C – H bond. Electron-withdrawing substituents enhance the reaction; thus, acrylates are ideal [25].

Reaction Mechanism

The mechanism involves organopalladium intermediates. The Pd(0) compound required in this cycle is generated in situ from a Pd(II) precursor [26][27].



Source: https://en.wikipedia.org/wiki/Heck_reaction

$Pd(OAc)_2$ is reduced by triphenylphosphine to bis(triphenylphosphine)palladium(0) [1] and triphenylphosphine is oxidized to triphenylphosphine oxide. Step **A** is an oxidative addition

in which Pd inserts itself in the aryl to bromide bond. Pd then forms a π-complex with the alkene(**3**) and in step **B** the alkene inserts itself in the Pd-C bond in a syn-addition step. Then follows a torsional strain relieving rotation to the trans isomer (not shown) and step **C** is a beta-hydride elimination (here the arrows are showing the opposite) step with the formation of a new palladium - alkene π complex (**5**). This complex is destroyed in the next step. The palladium(0) compound is regenerated by reductive elimination of the palladium(II) compound by potassium carbonate in the final step, **D**. In the course of the reaction the carbonate is stoichiometrically consumed and palladium is truly a catalyst and used in catalytic amounts. A similar palladium cycle but with different scenes and actors is observed in the Wacker process.

Ionic liquid Heck Reaction: In the presence of an ionic liquid, a Heck reaction proceeds in absence of a phosphorous ligand. Heck coupling of aryl halides or benzoic anhydride with alkenes can be performed with excellent yields in room-temperature ionic liquids, which provide a medium that dissolves the palladium catalyst and allows the product and by-products to be easily separated. Consequently, the catalyst and ionic liquid can be recycled and reused. In order to overcome the difficulties caused by the non-recovery of Pd at the end of the Heck reaction, can be overcome by using ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]), which are particularly insoluble in water and alkanes but readily dissolve many transition metal catalysts. Such biphasic ionic liquid systems have been used to enable simple extraction of products. Furthermore, if benzoic anhydride is used as a source of aryl moiety, then a base is not required for the reaction (the by-product in this case is an aryl carboxylic acid which can be recovered at the end of the reaction and converted back to an anhydride) [29].

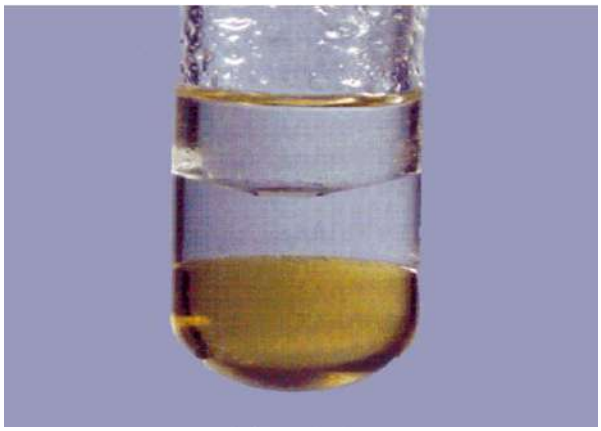
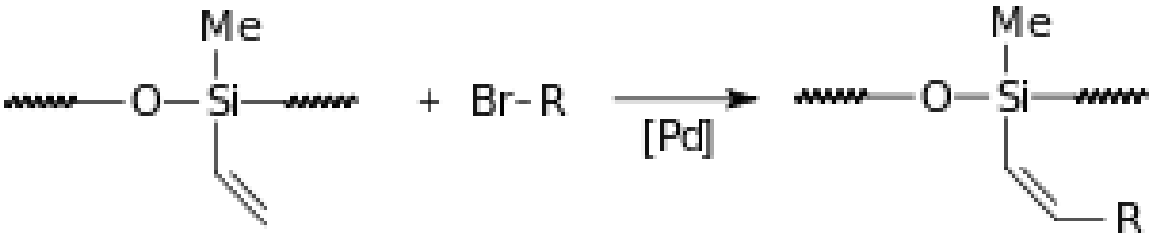


Figure 1. A triphasic mixture of $[bmim]_2[PdCl_4]$ and $P(o\text{-}tol)_3$ in $[bmim][PF_6]$ (lower layer), water (middle layer), and cyclohexane (top)

Source: Org. Lett., Vol. 1, No. 7

Heck coupling of aryl halides or benzoic anhydride with alkenes can be performed with excellent yields in room-temperature ionic liquids, which provide a medium that dissolves the palladium catalyst and allows the product and byproducts to be easily separated. Consequently, the catalyst and ionic liquid can be recycled and reused. The Heck reaction can also be performed in a number of low melting N,N' – dialkylimidazolium or N-alkylpyridinium ionic liquids with halide, hexafluorophosphate or tetrafluoroborate anions.

In one modification, $Pd(OAc)_2$ and the ionic liquid are immobilized inside the cavities of reverse phase silica gel[28]. In this way, the reaction proceeds in water and the catalyst is re-usable.



Source: https://en.wikipedia.org/wiki/Heck_reaction

In the Heck reaction of iodobenzene with ethyl acrylate (Table 1), the reaction proceeds smoothly to produce the expected *trans*-ethyl cinnamate in excellent yields[30]. For reactions carried out in the chloride salts (entries 1, 2, and 6-10), the N-hexylpyridinium salts give rise to higher yields than the corresponding reactions in imidazolium salts. The addition of a phosphine ligand to the palladium species in the reaction in the pyridinium salt decreased the yield, and a higher reaction temperature was then required to force the reaction to completion (entries 6 and 7). Several authors have reported that a cosolvent such as DMF or N-methylpyrrolidinone (NMP) is required for this reaction;4,17 however we have found that they are not required and can often decrease the yield of the reaction (entry 10).

For the reactions carried out in hexafluorophosphate or tetrafluoroborate room-temperature ionic liquids (entries 3 and 4), higher reaction temperatures are needed. Of these two anions, the tetrafluoroborate ionic liquid gives higher yields. In contrast to the chloride-based systems, the addition of a phosphine ligand (such as Ph3P) was found to promote the reaction in the imidazolium salt [bmim][PF6] (entry 5). This ionic liquid/catalyst combination can operated under triphasic conditions and give ethyl cinnamate in greater than 95% yield over

many reaction cycles, without loss of catalytic activity.

Table 1. Heck Reaction of Iodobenzene and Ethyl Acrylate To Give *trans*-Ethyl Cinnamate in Ionic Liquids with 2 mol % of $Pd(OAc)_2$

entry	ionic liquid	additive	base	temp, °C	time, h	yield, %
1	$[C_6py]Cl$	none	Et_3N	40	24	99
2	$[C_6py]Cl$	none	$NaHCO_3$	40	24	98
3	$[C_6py][PF_6]$	none	$NaHCO_3$	80	72	42
4	$[C_6py][BF_4]$	none	$NaHCO_3$	80	72	99
5	$[bmim][PF_6]$	Ph_3P (4 mol %)	Et_3N	100	1	95–99[19]
6	$[C_6py]Cl$	Ph_3P (4 mol %)	$NaHCO_3$	40	24	82
7	$[C_6py]Cl$	Ph_3P (4 mol %)	$NaHCO_3$	100	24	99
8	[pmim]Cl	none	Et_3N	80	72	10
9	[pmim]Cl	none	$NaHCO_3$	100	24	19
10	$[C_6py]Cl$	DMF	$NaHCO_3$	40	24	77

Source: Carmichael, Adrian J.; Earle, Martyn J.; Holbrey, John D.; McCormac, Paul B.; Seddon, Kenneth R. (1999). *The Heck Reaction in Ionic Liquids: A Multiphasic Catalyst System. , 1(7), 997–1000.*

To test whether less reactive aromatic compounds could reliably undergo the Heck reaction, the reaction of 4-bromoanisole (the relative reactivity in the Heck reaction is as follows: 4-(MeO)C_6H_4Br < PhBr < 4-(CHO)PhBr [31] with ethyl acrylate was investigated, in the ionic liquid [bmim][PF_6], using triethylamine as the base and a range of Group 15 ligands (Table 2). The reactions were carried out at two temperatures: 100°C and 140°C. As expected, the Group 15 ligand on the Pd catalyst had a significant effect on the yield and conditions required to complete the reaction. As shown in Table 2, three of the ligands chosen were unsuitable for this reaction, giving poor yields. These were triphenyl phosphite, triphenylstibine, and 1,2-bis(diphenylphosphino)ethane (entries 19, 21, and 27). In the case of triphenylstibine and 1,2-bis(diphenylphosphino)ethane, the palladium catalyst formed inactive insoluble complexes. As for the other reactions, over 94% yields were readily obtained at 140 °C. Two of ligands gave rise to reactions with rates lower than those in the absence of added ligand (entries 13- 17).21 The ligands triphenylphosphine and tri-o-tolylphosphine gave rate enhancements over the absence of Group 15 ligand at 100 °C. It

should be noted that in the case of tri-o-tolylphosphine, a palladacycle17b,22 has been observed from the reaction of tri-o-tolylphosphine and palladium(II) acetate, and this species may be the active catalyst. These observations appear to show that the electron rich or bidentate ligands reduce the reactivity of the catalyst. In the case where no ligand was present, the reaction was not effective at 100 °C. This is thought to be due to the formation of palladium black. At the higher reaction temperature of 140 °C, the palladium redissolves and the reaction proceeds smoothly. This order of reactivity is summarized in Figure 2.

Table 2. Heck Reaction of 4-Bromoanisole and Ethyl Acrylate To Give Ethyl 4-Methoxycinnamate with Various Group 15 Ligands in [bmim][PF_6] with Triethylamine as the Base

entry	Group 15 ligand added (4 mol %)	temp, °C	time, h	yield, %
11	none	100	20	7
12		140	18	94
13	triphenylphosphine	100	72	65
14		140	24	98
15	tri-*o*-tolylphosphine	100	4	55
16		100	24	65
17		140	18	99
18	triphenyl phosphite	100	24	1.5
19		140	24	31
20	1,2-bis(diphenylphosphino)ethane[27]	100	18	< 1
21		140	24	13
22	1,1′-bis(diphenylphosphino)ferrocene[27]	100	18	< 1
23		140	18	95
24	triphenylarsine	100	12	2
25		140	20	99
26	triphenylstibine	100	72	< 1
27		140	24	24

Source: Carmichael, Adrian J.; Earle, Martyn J.; Holbrey, John D.; McCormac, Paul B.; Seddon, Kenneth R. (1999). *The Heck Reaction in Ionic Liquids: A Multiphasic Catalyst System.* , *1(7), 997–1000.*

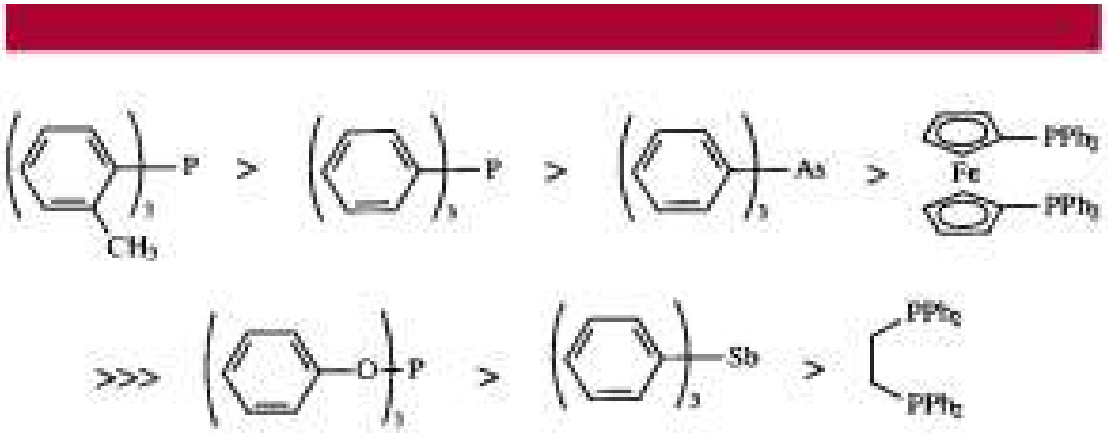


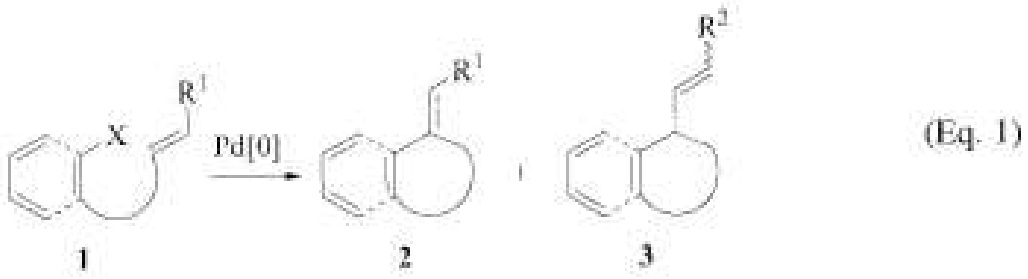
Figure 2. The relative order of reactivity for different ligands in the Heck reaction at 100 °C (Table 2).

[39]

Source: Carmichael, Adrian J.; Earle, Martyn J.; Holbrey, John D.; McCormac, Paul B.; Seddon, Kenneth R. (1999). *The Heck Reaction in Ionic Liquids: A Multiphasic Catalyst System. , 1(7), 997–1000.*

Intramolecular Heck Reaction (IMHR)[32]

Since the discovery of the Heck reaction, the process has gained widespread acceptance within the synthetic community both as a practical tool and a research area. The intramolecular Heck reaction has enjoyed a similar renaissance, particularly within the last decade. The reaction has emerged as a reliable method for efficiently constructing small, medium and large rings and is outlined in generic form in Eq. 1 (1 → 2 and/or 3). Since the reaction occurs under mild and nearly neutral conditions, the functional group tolerance is high.



(Eq. 1)

Source: Link, J. T. (2004). *Organic Reactions || The Intramolecular Heck Reaction. , 10.1002/0471264180(), –.*

Tandem reactions, which are initiated by intramolecular Heck reactions, have been developed allowing for multiple ring formations, cyclization and intermolecular coupling, and a multitude of other ever-expanding possibilities. Furthermore, congested tertiary and

quaternary centres can be efficiently constructed diastereoselectively or enantioselectively during the ring formation reaction.

Mechanism and Stereoselectivity

The Neutral Pathway

As shown in Eq. 2, the neutral pathway of the Heck reaction begins with the oxidative addition of the aryl or alkenyl halide into a coordinatively unsaturated palladium(0) complex (typically bound to two phosphine ligands) to give complex **I**. Dissociation of a phosphine ligand followed by association of the alkene yields complex **II**, and migratory insertion of the alkene into the carbon-palladium bond establishes the key carbon-carbon bond.

Insertion takes place in a suprafacial fashion, but the dihedral angle between the alkene and palladium-carbon bond during insertion can vary from 0° to ~90°. After insertion, β-hydride elimination affords the product and a palladium(II)-hydrido complex **IV**, which is reduced by base back to palladium(0)[33].

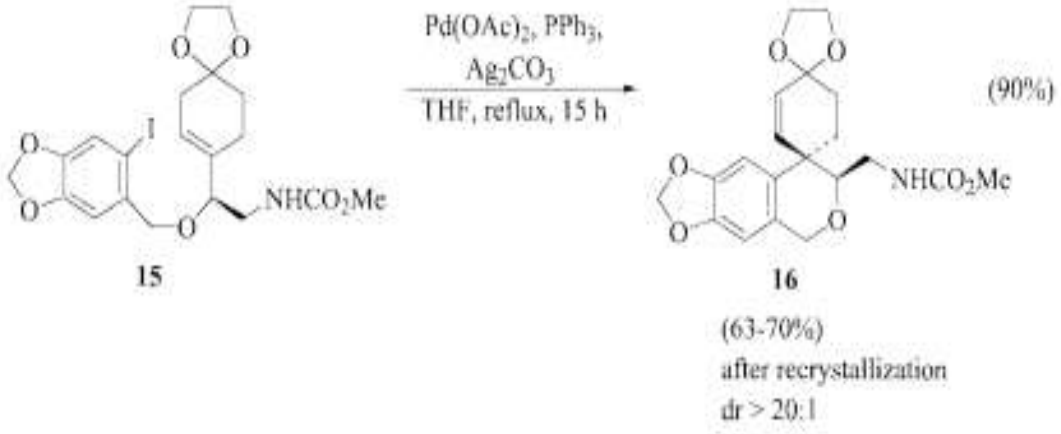
The Cationic Pathway

Most asymmetric Heck reactions employing chiral phosphines proceed by the cationic pathway, which does not require the dissociation of a phosphine ligand. Oxidative addition of an aryl perfluorosulfonate generates a cationic palladium aryl complex **V**. The mechanism then proceeds as in the neutral case, with the difference that an extra site of coordinative unsaturation exists on palladium throughout the process.

Thus, coordination of the alkene does not require ligand dissociation. Stoichiometric amounts of base are still required to reduce the palladium(II)-hydrido complex **VIII** back to palladium(0).[34] Silver salts may be used to initiate the cationic pathway in reactions of aryl halides.[35]

Aryl and vinyl perfluorosulphates react via this mechanistic pathway. Cyclization of substrates that can access either insertion orientation has been conducted (Eq 3). For example, aryl iodide upon treatment with a catalyst derived from from $Pd(OAc)_2$ and triphenylphosphine, in the presence of silver carbonate, yields cyclic ether in good yield. The

diastereoselectivity of the reaction, which proceeds via the cationic pathway, is greater than 20:1 [36].



(Eq. 3)

Source: Link, J. T. (2004). *Organic Reactions || The Intramolecular Heck Reaction. , 10.1002/0471264180(), –.*

The Anionic Pathway

Reactions involving palladium(II) acetate and phosphine ligands proceed by a third mechanism, the anionic pathway[38]. Base mediates the oxidation of a phosphine ligand by palladium(II) to a phosphine oxide. Oxidative addition then generates the anionic palladium complex **IX**. Loss of halide leads to neutral complex **X**, which undergoes steps analogous to the neutral pathway to regenerate anionic complex **IX**. A similar anionic pathway is also likely operative in reactions of bulky palladium tri(*tert*-butyl)phosphine complexes[37].

Conclusion

The last couple of decades have seen a huge leap in the development of medically and biologically important compounds which have been synthesized artificially and at economical conditions. Transition metal catalysts and the recent developments in the field of chemistry has enabled organic chemists to utilize them to synthesize parts of or the entire compound. These reactions, specially the Mizoroki – Heck reaction is one important milestone in achieving this feat and thus was the recipient of the Noble Prize in Chemistry in 2010. Pd catalyst supported on zeolites and Pd-nanoparticles have specifically increased the selectivity of the reaction sites as well as the stereocentres. The most important use of Pd-catalysts to this day still remains the production of hydrogen from formic acid and its immense number of applications in various reactions such as the Heck, Suzuki, Negishi reaction which are very important in production of artificial biological and medicinal products.

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HIGHLY CONCENTRATED ACIDIC SALT SOLUTION: A NEW SUBSTITUTE OF AQUA REGIA

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. SOUGATA SARKAR

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DATE: 05-01-2022

PLACE: RAHARA

HIGHLY CONCENTRATED ACIDIC SALT SOLUTION: A NEW SUBSTITUTE OF AQUA REGIA

ABSTRACT:

Highly concentrated solutions of $AlCl_3 \cdot 6H_2O$ and Al $(NO_3)_3 \cdot 9H_2O$ can be used for gold and platinum group metals dissolution instead of Aqua regia (a mixture of concentrated nitric acid and concentrated hydrochloric acid in a 1:3 volume ratio) which is a potentially dangerous solvent mixture and not environment friendly.

The review article based on the substitute of aqua regia i.e. the mixture of $AlCl_3 \cdot 6H_2O$ and Al $(NO_3)_3 \cdot 9H_2O$ .It is used as a leaching agent ,95% Pd was leached from spent automotive catalysts in 15 min at 80 °C, while Pt required longer times; Rh dissolution was <20%. Au dissolution from wires required 24 h. Pd recovery was investigated by reductive precipitation. It dissolves noble metals at a much greater rate than can be achieved with boiling Aqua regia.

INTRODUCTION:

Aqua regia is well known leachant used in hydrometallurgy to selectively extract gold, platinum, palladium etc. Several recycling processes to recover precious metals from electronic scrap and spent catalysts make use of aqua regia. Aqua regia is very dangerous solvent mixture though it is used still in laboratories.

In these circumstances, scientists figure out some substitutes of aqua regia. For instance, Organic aqua regia, which is composed of thionyl chloride ($SOCl_2$) and a polar aprotic organic solvent such as pyridine, imidazole or *N*, *N*-dimethylformamide (DMF), has been proposed as a safer alternative for aqua regia. Some researcher proposed $FeCl_3$–KCl mixture as dry aqua regia, some proposed aluminium chloride solution with low concentration of nitric acid can be used instead of aqua regia for the recovery of platinum from spent automotive catalysts(Spent catalysts are an excellent source of secondary platinum since they contain the metal in considerably higher concentrations than the ores from which it is extracted. The researchers have taken that next step and shown that highly concentrated solutions of aluminium chloride and aluminium nitrate can also readily dissolve gold as well as the platinum group noble metals.

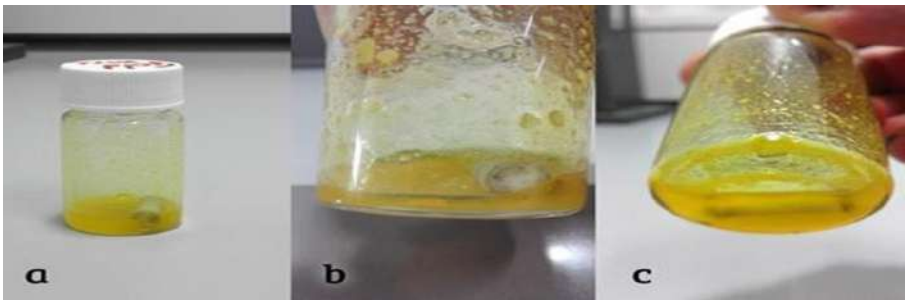
They prepared a concentrated mixture of hydrated $AlCl_3$ and $Al(NO_3)_3$ with ratios of 75–85 wt% hydrated salts to 15–25 wt% water and tested the solutions on metal wires and spent automotive catalysts.

SUMMARY OF THE PROJECT WORK:

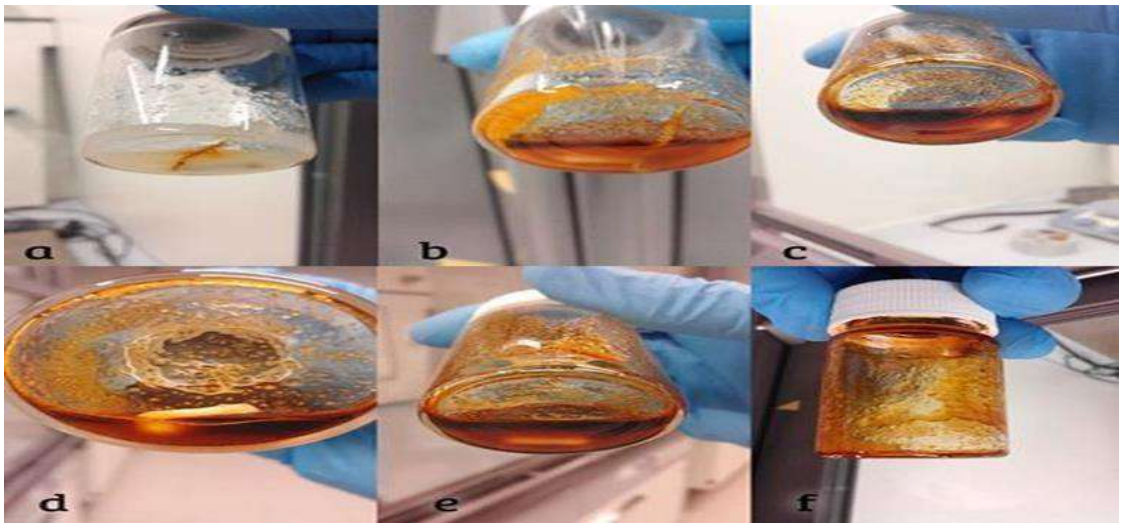
Concentrated solution of highly valent metal salts having H_2O : Metal ion ratio sufficiently low to minimise outer sphere hydration would show a marked degree of acidity which can be utilised to dissolution of Noble metals. Such highly concentrated salt solutions have a limited amount of free water molecules and are closely related to molten salt hydrates.

In this context, a concentrated mixture of hydrated $AlCl_3$ and $Al(NO_3)$ is used as leaching agent. The recovery of platinum group metals from the leachate was explored by reductive precipitation with ascorbic acid. The researchers suggest that a multi-stage leaching process might be employed, with fresh solvent used each time to boost the dissolution of platinum and rhodium.

LEACHING PROCESS: Preliminary leaching tests were performed on palladium wires by using the following conditions: salt/wire (S/W) ratio = 35 g/g, T = 80 °C, stirring speed = 350 rpm. Equal amounts of hydrated $AlCl_3$ and $Al(NO_3)_3$ were used in each experiment. After some times the palladium wires stated to dissolve and the whole leachate turned into reddish. Full dissolution is observed after 4.5 hr. The same conditions are applied for dissolution of gold wire. But this time the full dissolution is observed after 24 hr due to higher thickness of gold wire compared to palladium. Extra tests were performed on platinum and rhodium wires. It was found that Pt was fully dissolved after a couple of days whereas the Rh wire could not be dissolved.



Gold wire in contact with the molten salt hydrate mixture after 3 hours (a), 5 hours (b) and 24 hours (c) leaching



Palladium wire in contact with the molten salt hydrate mixture after 3 minutes (a), 1 hour (b), 2 hours (c), 3 hours (d), 4 hours (e) and 4.5 hours (f) leaching

The effectiveness of the leaching system was also tested consisting spent automotive catalysts. In terms of leaching efficiency, it gives highest yield for palladium dissolution. It is observed that full dissolution of all platinum group metals are not achieved easily but selectively palladium is observed to be fully dissolute in a short period of time.

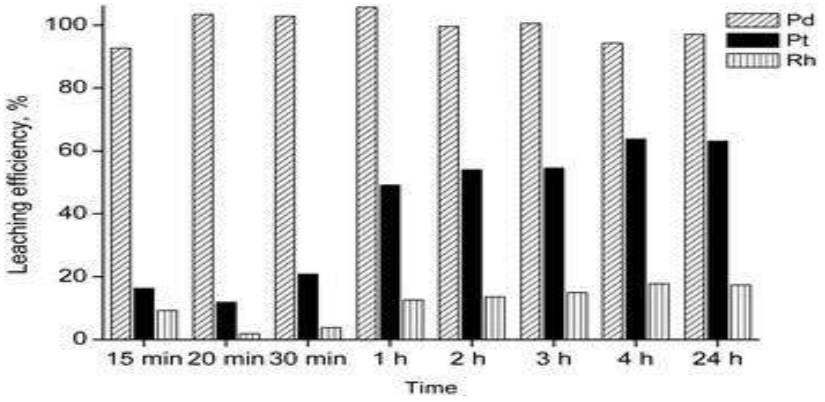


Fig: Leaching as a function of time (salt-to-catalyst ratio = 35 g/g, T = 80 °C, water added = 26 wt%, stirring speed = 350 rpm).

The leaching mechanism can be explained with the oxidation of metals by HNO_3; the oxidized ions then react with chloride ions resulting in hexachloroplatinate(iv) ($PtCl_6^{2-}$) ions

The chemical reactions are-

$$Pt_{(s)} + 4NO^{-}_{3(aq)} + 8H^{+} \rightarrow Pt^{4+}_{(aq)} + 4NO_{2(g)} + 4H_2O_{(aq)}$$

$$Pt^{4+}_{(aq)} + 6Cl^{-}_{(aq)} + 8H^{+} \rightarrow PtCl^{2-}_{6(aq)}$$

Leaching requires an oxidising agent (here HNO_3). Its reduction potential is high enough to allow the oxidation reaction to take place. The leaching mechanism is mainly based on the dissolution of Pt and the formation of its hexachloroplatinate complex at pH<1 as at higher pH the complexes may hydrolyse forming hydroxy complexes.

From the above leaching process we have seen that the leaching of palladium is the fastedt and easiest one as the electrochemical potential of palladium is high and the stability of chloropalladate(ii) complexes are also high at low pH.

RECOVERY OF METALS: The recovery of palladium was investigated by reductive precipitation with ascorbic acid. At first precipitation tests were performed on a leachate obtained from the dissolution of palladium wire. Equal volumes of the leachate and a solution of ascorbic acid in water were contacted. Samples were shaken for 5 min and afterwards allowed to settle at room temperature. At first, no changes to the solution were observed, but after three days, a metallic precipitate was found on the bottom of the vial . In order to determine its composition, the precipitate was washed with water, dried (T = 105 °C, t = 2 h) and re-dissolved in 65% HNO_3 for ICP analysis. As expected from the reductive potentials of palladium and aluminium, only palladium was precipitated from the leachate, while aluminium remained in solution. Standard reduction potentials ($E°/V$) are −1.662 for Al/Al^{3+} and +0.951 for Pd/Pd^{2+}. . The palladium precipitation reaction can be express as:

$$Pd^{2+} + H_2A \leftrightarrow Pd_{(s)} + A + 2H^{+}$$

CONCLUSION:

In conclusion, highly concentrated solutions comprising mixtures of hydrated aluminium nitrate and chloride salts were tested for the dissolution of platinum group metals . The leaching system was tested both on metal wires and on real material (spent automotive catalysts). Quantitative dissolution of palladium from the catalysts powder was achieved in a short time (15 min); about 64% platinum can be dissolved when the contact time is increased up to 4 h. Further investigation is required in order to optimize PGMs recovery via reductive precipitation with ascorbic acid.

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29. Dissolution of noble metals in highly concentrated acidic salt solutions: Federica Forte , Sofia Riaño and Koen Binnemans ,Royal society of chemistry
30. Figure source:Koen Binnemans/KU Leuven

CARBOHYDRATES AND DRUG DESIGN

Project Work

Submitted as Partial Fulfillment of the B. Sc Degree in Chemistry

By

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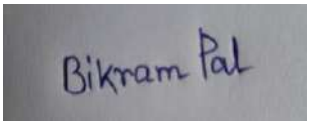

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ABSTRACT:

Carbohydrates and glycoconjugates are involved in several biological processes including host-pathogen interactions, cell communication, proliferation and differentiation as well as the initiation of immune responses. Recent advances in glycochemistry and glycobiology have helped elucidate the biological functions of carbohydrates.

This review illustrates the impact of carbohydrates synthesis on the design of efficient carbohydrates-based anti-diabetic, anti-tubercular, anti-parasitic, anti-HIV, and carbohydrate-based mettallo drugs etc. In addition, this review focuses on how immunological research might benefit from glycochemistry's novel techniques.

INTRODUCTION:

Carbohydrates are the most abundant and easily accessible natural products. Although, their extraordinary chemical significance lies in their unique structural traits, such as the presence of multiple hydroxy groups, simple yet firm structure and chirality. Sugar is an excellent energy source and serves as an energy storage molecule. Carbohydrates are an essential part of any biological system and process. For example, ribose sugar is a necessary part of genetic materials (nucleic acid); carbohydrates serve as antigens and play a significant role in deciding the blood group. Heparin acts as a natural anticoagulant in blood. Naturally occurring carbohydrates and chemically modified oligosaccharides' structure promises to impact the glycobiology field significantly. Case studies documented successful application of carbohydrates as an active agent, for example, fully synthetic oligosaccharide vaccine to combat tropical disease (e.g., malaria), bacterial infections (e.g., tuberculosis), viral infections such as HIV and cancer.

DISCUSSION:

A good drug is a target-specific drug; users can expect high efficiency and few side effects. Target-specificity also means recognition, and this is where carbohydrates come in. These aspects of carbohydrates in drug design, with transition in glycobiology, mainly when biological mechanisms and their manifestation in vivo are considered. This chapter introduces the following six categories, described below:

1. Carbohydrate-based anti-diabetic drug:
2. Carbohydrate-based anti-tubercular drug
3. Carbohydrate-based anti-parasitic drug
4. Carbohydrate-containing molecule as anti-HIV agent
5. Carbohydrate-based mettalo drugs
6. Carbohydrate based vaccines

1. Carbohydrate-based anti-diabetic drug

Diabetes mellitus has a globally spread health issue that has emerged as a significant cause of concern because of related mortality rates. Type II diabetes mellitus which is the most common type of diabetes, is described as a condition in which the course of processing of blood sugar (glucose) by the body is affected. Type II diabetes mellitus causes declines in insulin secretion, in addition to insulin resistance in peripheral tissues which in turn causes hyperglycemia, an increase in blood glucose level. Therapy often involves the identification of specific targets that affect glucose metabolism and their modulation

Glycosidase inhibitor with anti-diabetic effect:

It has been recently presented the scope of carbohydrate-containing molecules in managing Type II diabetes. Sugar-based glycosidase inhibitors and sodium-glucose co-transporter 2(SGLT2) inhibitors were considered the major active classes of molecules for the management of diabetes. Many glycosides inhibitors help control the blood sugar level.

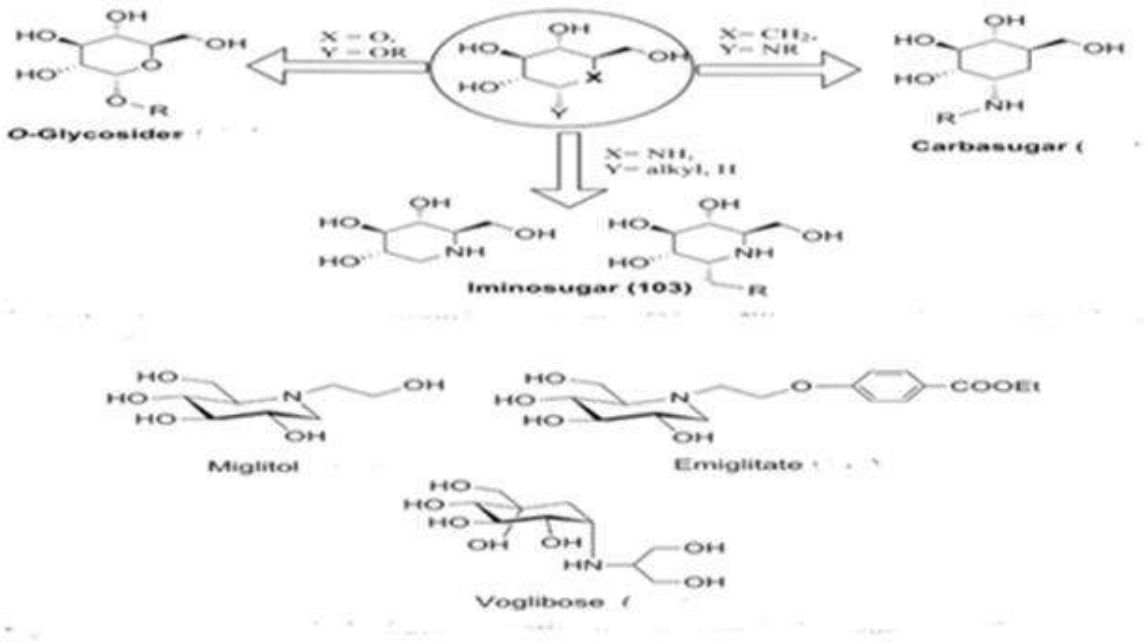

Figure.1. Carbohydrate-based anti-diabetic drugs

2. Carbohydrate-based anti-tubercular drug

Many novel specific target-based anti-tubercular drugs have been developed so far that target biosynthesis of nucleic acids or protein, DNA topoisomerase, enzyme etc. Enzyme and genetic materials, which play a crucial role in the biosynthesis of saccharides on the cell wall of TB bacteria, are a most exciting target for anti-tubercular drug development and instigate to development of a novel drug to fight TB. Interestingly, the presence of a cell wall in the bacterial cell and the absence of a cell wall in the host cell make biosynthesis of the mycobacterial cell wall a critical molecular target for designing and developing antibacterial agents. The plasma membrane of M. tuberculosis's wall is primarily composed of furanose polysaccharides. The mycolyl- arabinogalactan peptidoglycan complex, which aids in the synthesis of lipoarabinomannan (LAM) and arabinogalactan (AG) with the furanose form of arabinose and galactose residue, respectively, is essential for mycobacterial cell wall formation. Restriction of the biosynthetic of LAM and AG is the target factor that can help in the design and development of a novel anti-tubercular drug, for example, Rifampicin, Pyrazinamide etc.

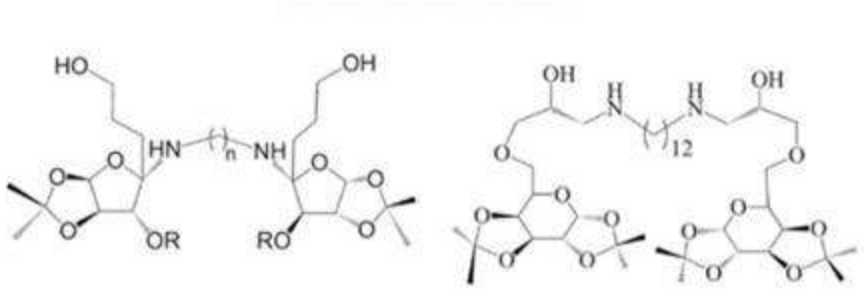

Figure.2. Anti-tubercular drugs (Galactopyranosyl alcohol, N, N-digalactopyranosylated amino alcohol)

3. Carbohydrate-based anti-parasitic agents

Antiparasitics is a category of drugs that are used for the cure against parasitic disease, like those caused by protozoa, ectoparasites, amoeba etc. Many carbohydrates -derivatives have been found active against this type of disease. Leishmaniasis is a disease caused by Leishmania parasites. Available anti-leishmanial therapies include a combination of paromomycin, pentavalent miltefosine and Amphotericin B etc.

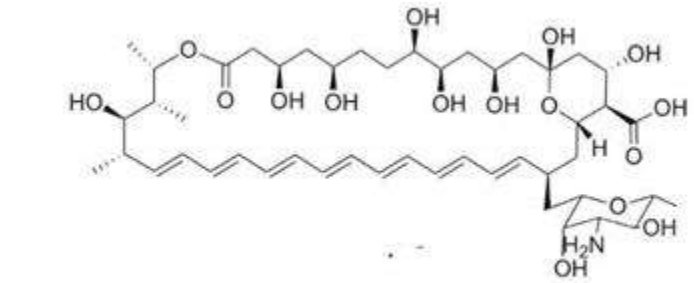

Figure. 3. Carbohydrate-based anti-parasitic drugs (Amphotericin B, a drug for visceral leishmaniasis)

4. carbohydrate-containing molecules as anti-HIV agents:

Acquired immunodeficiency syndrome (AIDS) is one of the fatal diseases with the highest mortality rate. The cause of AIDS is the human immunodeficiency virus (HIV) by which helper T –cells are affected which in turn breaks down the immune system and the carrier become vulnerable to a wide array of infection. The main target of potential anti-HIV agents is the reverse transcriptase (HIV-RT) enzyme which is involved in viral replication. A library of benzene 1,2,3-triazole derivatives was developed and assessed biologically for activity against HIV-RT.

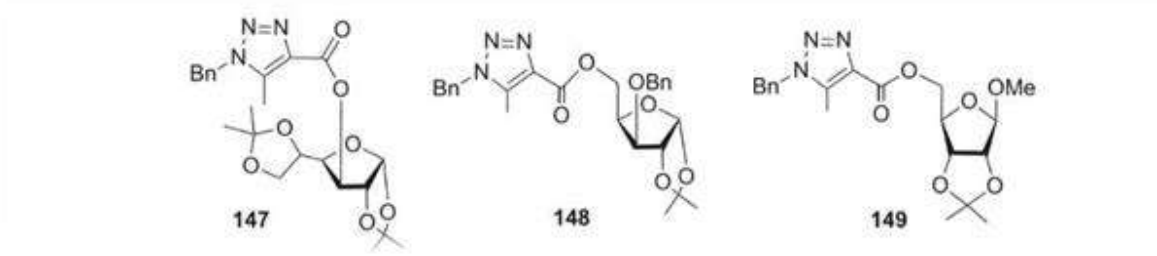

Figure. 4. Anti-HIV-RT glycosyl triazoles

5. Carbohydrate-based metallodrugs:

The therapeutic value of carbohydrate-containing metal complexes results from amalgamating two actives, the first comes from metal ions, and the other comes from carbohydrates ligand. These complexes show low toxicity, biocompatibility, water solubility, and uptake enhancement. Platinum complexes of carbohydrate-derive ligands (Figure 5) have been explored mainly in tumor therapy. The uptake of glucose and derivatives by growing tumor cells increases due to GLUT 1-4 on the cell membrane. Other reported antitumor activity carbohydrate-platinum complexes.

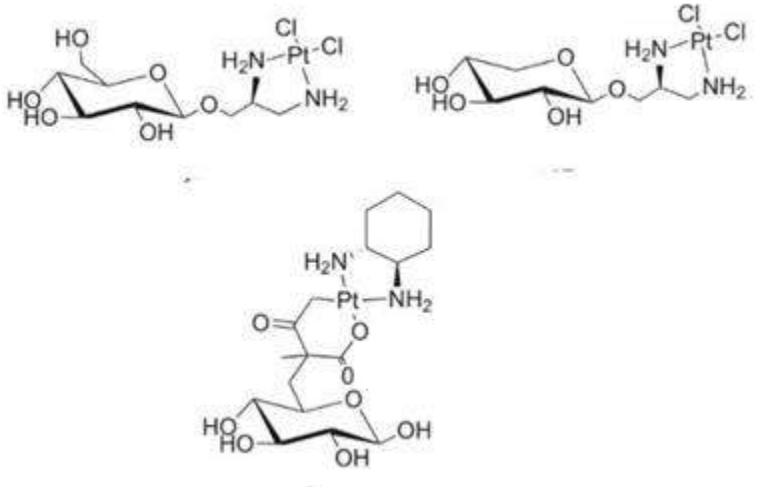

Figure.5. Pt-complexes of Carbohydrate derivatives with antitumor/anti-cancer activity

6. Carbohydrate-based vaccines:

Vaccines are preventive measures that provide active acquired immunotherapy and hence are sometimes considered better than drug-based therapy because of related drug resistance issues. The presence of carbohydrates on the surface of the host, as well as pathogen in a specific away, offers them a suitable candidate based on which vaccines against a particular disease can be developed. The first carbohydrate-based vaccine was created in 1983 from Pneumovax; a capsular polysaccharide Pneumovax used to prevent pneumonia. Prevnar is a Pneumococcal conjugate vaccine used against pneumonia caused by Streptococcus pneumonia. Another example is Theratope, a (Sialyl Tn Ag) conjugate vaccine developed as immunotherapy against metastatic colorectal and breast cancer.

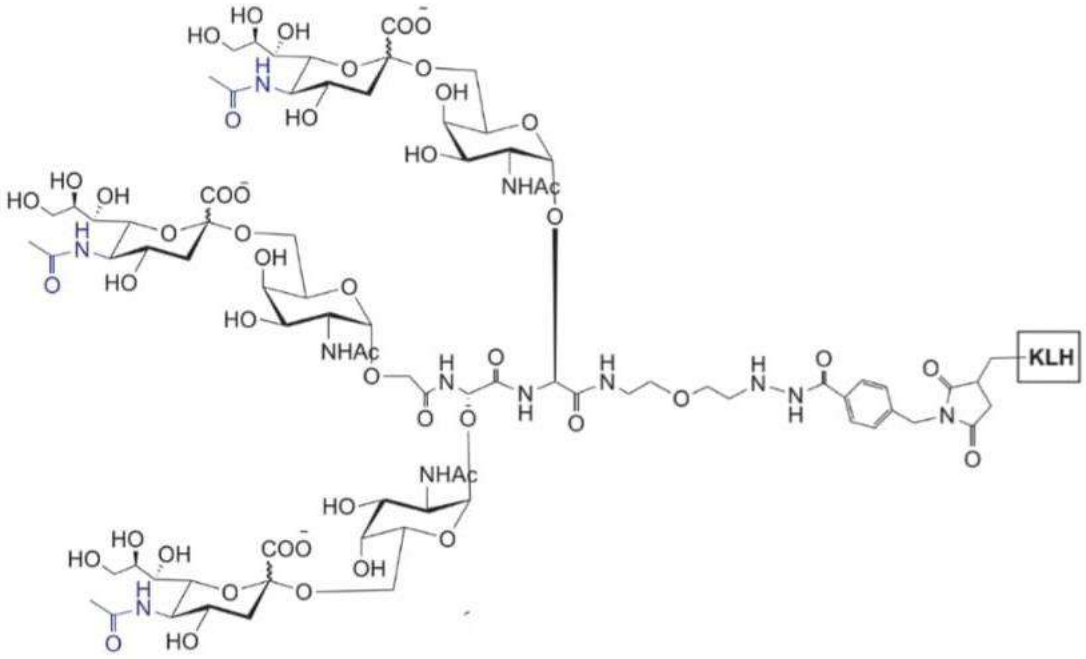

Figure.6. Theratope, a(Sialyl Tn Ag) is a conjugate vaccine against breast cancer

CONCLUSION:

Carbohydrates, one of the abundant and widespread biomolecules in nature, play an indispensable role in diverse biological functions and represent a treasure trove of untapped potential for pharmaceutical application. Carbohydrate-based bioactive entities, including polysaccharides/oligosaccharides, small molecule glycosides, glycomimetics, and more complex carbohydrates such as glycoproteins and derivatives, have shown great potential in drug development. Especially in terms of polysaccharides and oligosaccharides, marine organisms have proven to be a good resource for searching and developing novel pharmaceuticals. Carbohydrate digital databases and entity libraries, combined with the recently approved drugs and emerging techniques summarized herein, will inspire new sights into potential opportunities to discover novel carbohydrate drugs.

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INHIBITION OF SOME ZINC CONTAINING METALLOENZYMES AND THERE APPLICATION

Project Work

Submitted for Partial Fulfilment of the B.Sc Degree in Chemistry

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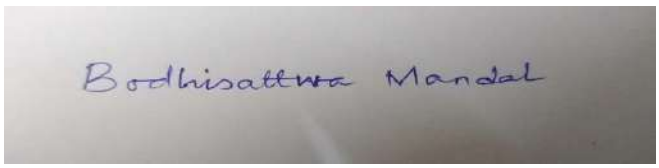

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INHIBITION OF SOME ZINC CONTAINING METALLOENZYMES AND THEIR APPLICATION

ABSTRACT:

Metalloenzymes occupy a large portion of enzymes which have very wide range of usage, such as in DNA modification, protein homoeostasis, antibiotic resistance, and are used as target element for different drugs. Platinum based anticancer drugs are quite successful in curing cancer but their problem is they target DNA which have huge side effects and drug resistance is also built easily in this process.

It is seen that zinc-containing metalloenzymes contribute largely in occurrence and development of cancer so they are being used as target for different metal complexes which are anticancer drugs. Metal complexes have some suitable features for the enzyme inhibition, such as, 1) For enzyme-binding selectivity and to increase affinity 3D structure is required which is present in metal complexes 2) Due to redox activity enzyme inhibitors can be designed with multiple modes of action.

Here some zinc based metalloenzymes are discussed which are efficient as well as have less side effect. Mainly here four zinc-containing metalloenzymes are discussed- histone deacetylases (HDACs), carbonic anhydrases (CAs), and matrix metalloproteinases (MMPs).

INTRODUCTION:

Many platinum-based anticancer drugs such as cisplatin, carboplatin etc. are used in the treatment of ~50%-70% of cancers (Bruno et al.2017). But drug resistance is made very easily in this case and they have side-effects which is a great barrier towards the development of these drugs (Galluzzi et al.2012). Due to this reason alternative pathways for cancer treatment is in search.

More than 30% of all enzymes are metalloenzymes. Various small drug molecules target enzymes and show their therapeutic effect. So, on an average about one-third of all drugs

should target metalloenzymes, but, according to recent review results less than 5% of small molecule drugs target metalloenzymes.[1] So, we can see that there is a huge gap between number of potential metalloenzyme targets and the number of drugs designed which are capable of choosing those metalloenzymes as target.

Metalloenzymes are essential in many biological processes so they can be used for treatment over a wide range of diseases. Many of them are used for the treatment of hypertension, glaucoma, cancer, HIV/AIDS[2] etc. They form covalent coordinate bond with the metal ion for the inhibition of their target. Different functional groups are used in these inhibition for the binding with the active site of metal ion namely chelator, metal-binding group(MBG) and zin-binding group(ZBG, for Zn-dependent metalloenzyme inhibitors). Here the term metal binding pharmacophore (MBP) is used for some valid reasons.

Now comes the problem with metalloenzymes. We have very less number of MBPs which have been used to bind the active site of metal ion. For a long time matrix metalloproteinases (MMPs), a class of Zn-dependent metalloenzyme is used for arthritis and cancer therapeutics. According to a review by Whittaker in 1999 many compounds showed apparent reliance on a particular MBP, hydroxamic acid functional group[3]. It is used for the inhibition of Zn-dependent MMPs. It is also used to construct different drugs.

SUMMARY OF THE WORK:

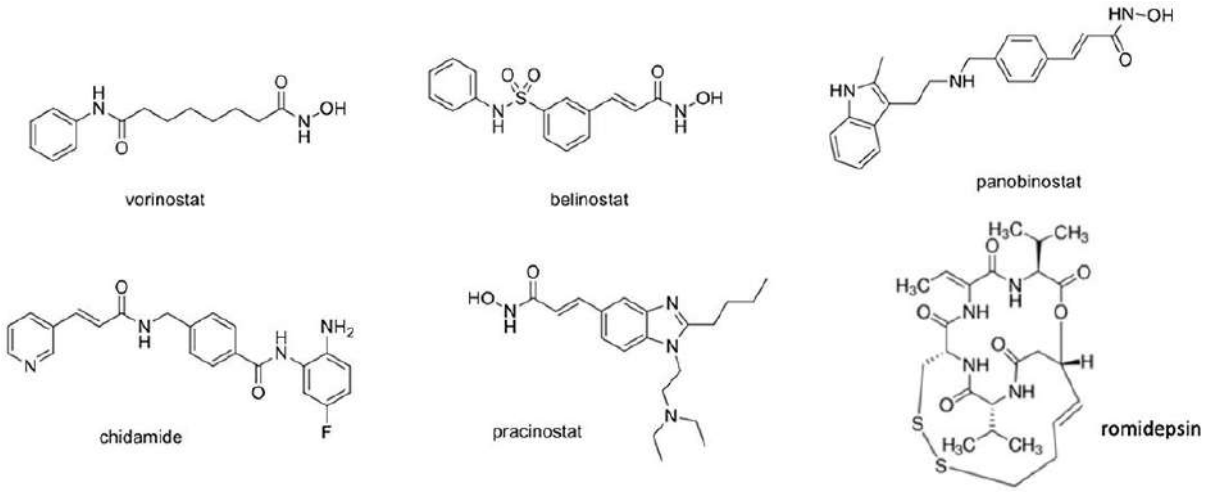
1)Histone deacetylases:

These are known as HDACs. They catalyse the deacetylation of lysine residues on histones and alter the chromatin structure to regulate the access to DNA[4]. There are total 18 HDACs and are of four types. Class I consists of HDAC 1,2,3 and 8, class IIA consists of HDAC 4,5,7 and 9, class IIB consists of HDAC 6 and 10, class III is called surtuins 1-7, class IV consists of HDAC 11 only. Except class III members all are metal dependent[5].These are used as targets for various drugs of cancer, fibrosis, metabolic disorders, autoimmune disease, inflammation[6], antifungal[7], antiaging[8] etc.

In general HDACs are classified into two categories – hydroxamic and non-hydroxamic. Some of the hydroxamate derivatives consist of the fragment of suberoylanilide hydroxamic

acid(SAHA, vorinostat) which was the first clinically approved HDAC inhibitor and was used for treatment of cutaneous T-cell lymphoma[9].

According to recent studies schistosomiasis is similar to cancer. Tumour like parasites show high metabolic activity and uncontrolled cell division. They utilize lactic acid as an energy source and are able to escape from immune surveillance. Schistosoma is basically a eukaryotic flatworm. In it's life cycle histone deacetylase is very important. Now, smHDAC is not as conservative as human HDAC8(hHDAC). So, HDAC8 can be a good target[10].



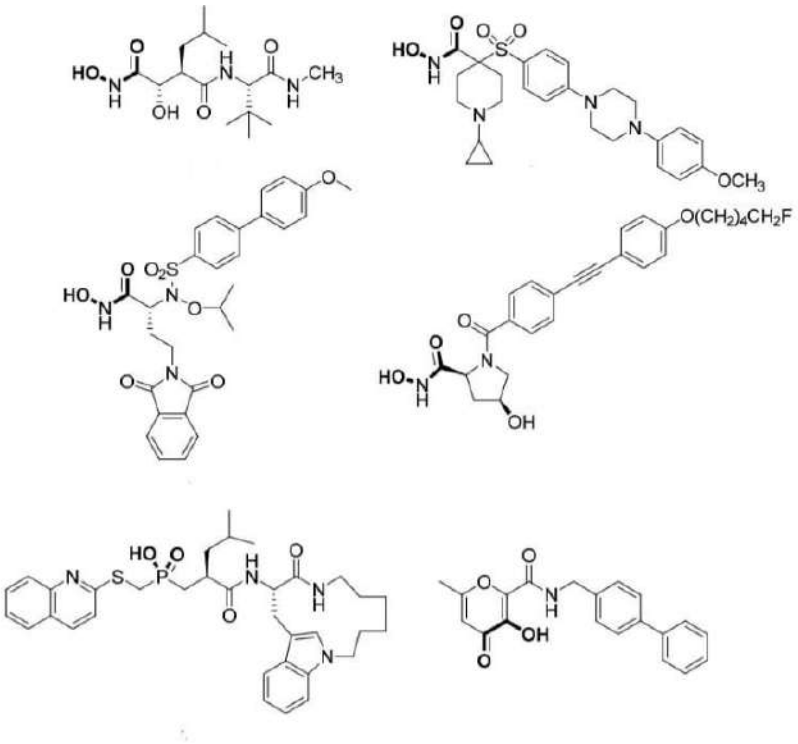
Different HDAC inhibitors having Zn^{2+} chelating group

2)Matrix metalloproteinases:

According to different studies it is seen that many Zn^{2+}-related proteases bind Zn^{2+} in a similar manner – HEXXHXXGXXH. These enzymes are classified into 7 types – astacins, adamalysins, serralysins, pappalysins, snapalysins, leoshimanolysins and matrix metalloproteins (MMPs)[11-13].

MMPs are Zn^{2+} dependent endopeptase. It contributes in the degradation of extracellular matrix and different cell membrane components such as, collagen, elastin, gelatin etc. On the other hand MMPs are responsible for the occurrence and development of different severe diseases like cancer[14], kidney diseases[15], HIV- related diseases[16] etc. MMPs can be classified in many classes depending upon different parameters.

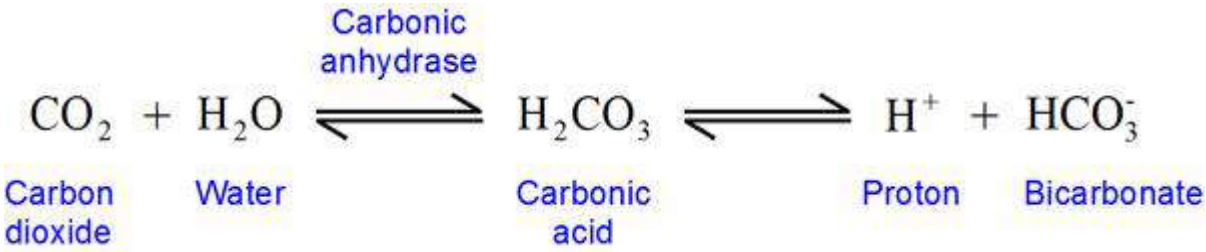
Many MMP inhibitors were developed but all were not equally successful. Recently different inhibitors with new ZBGs are developed. Nara and colleagues have designed a class of MMP-13 inhibitors that have 1,2,4-triazole -3-yl group as a ZBG. This group binds with Zn^{2+} via a coordinate bond in a monodentate manner[17]. Nguyen and co-workers have found a new selective MMP-2/9/14 inhibitor where Glu-404 is the active site which captures a proton. Due to this an ionized thioenol is formed which is tightly bound to the Zn^{2+}.[18]



Different MMP inhibitors containing Zn^{2+} chelating group

3)Carbonic anhydrases:

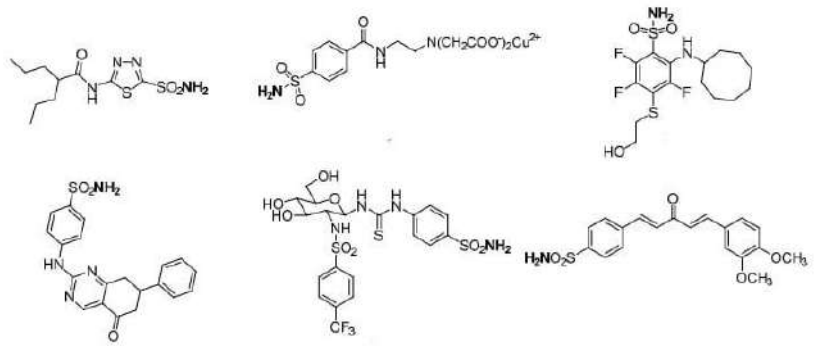
It is shortly known as CA. It is the first discovered Zn^{2+}-dependent metalloenzyme. It's major function is to catalyse the hydration reaction of carbon-di-oxide into carbonic acid.[19-20]



Carbonic anhydrase inhibitors (CAIs) are used for the treatment of glaucoma and cancer. By lowering the aqueous humor (AH) production glaucoma can be treated. Basically CAIs inhibit HCO_3^- production, as a result, the transport of HCO_3^- and its counter ion Na^+ from non-pigmented epithelium (NPE) to the posterior chamber is reduced. Due to this osmotic pressure difference between plasma and AH decreases and the passive flow of water into the posterior chamber is stopped[21-22]. CAs contribute largely in regulating the acid-base equilibrium in tumour cells. They protect the tumour cells by maintaining intercellular pH near physiological levels.[23]

CAs are found in most of the living beings. They are classified into many classes. Among them twelve isoforms can coordinate a zinc by their active site. Those are CAs I-IV, CAs VA-VB, CAs VI-VII, CA IX and CAs XII-XIV.[24]

Different types of CA inhibitors have been developed. Among them sulfonamide-containing compounds are major. According to quantum mechanical calculations sulphur atom binds with Zn^{2+} in a tetrahedral geometry.[25] Recent studies say that sulfonamides might be the best ZBG for the generation of good CAIs but in case of developing selective CAIs, structurally diverse ZBGs are possible.[26]



Different CAIs containing Zn^{2+} chelating group

CONCLUSIONS:

Medicinal application of Bioinorganic is comparatively new concept in the medicinal field. In a short time span bioinorganic drugs and metalloenzymes have shown success in some fields. It is tremendously successful in the treatment of HIV and some type of tumours and

cancers. Beside being successful in treatment it is also less harmful i.e. it has very less side effect. So, in coming days metalloenzymes are going to be very important in medical science. I hope my effort will help the readers to gain some knowledge about Zn-containing metalloenzymes.

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MODERN SYNTHETIC TOOL; L-PROLINE AS AN ORGANOCATALYST

Project Work

Submitted as Partial Fulfillment of the B.Sc. Degree in Chemistry

By

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Under the supervision of Dr. Kumar Ranabir Sur

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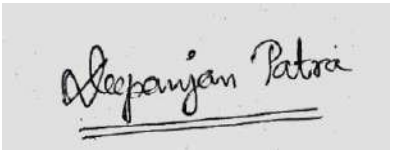

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MODERN SYNTHETIC TOOL; L-PROLINE AS AN ORGANOCATALYST

ABSTRACT:

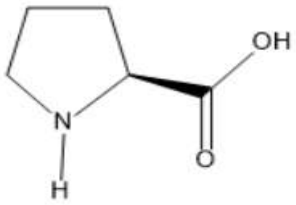
At present organocatalysis is a very efficient method in Synthetic Green Chemistry. In organocatalysis a sub-stoichometric amount of an organic compound which does not contain a metal atom used to accelerate the rate of a chemical reaction. In this context L-Proline is widely used as an organocatalyst due to its great potential for realizing highly complex, effective and selective asymmetric transformations. This project work provides an updated information on recent reports and explains usefulness of L-Proline organocatalysis and its efficiency for this approach and scope.

INTRODUCTION:

In organic synthesis when small organic molecules are used as catalyst then the reaction is said to be organocatalysis. The organocatalysts can easily form Lewis acids. They provide a strong tool for catalyzing reactions in the absence of transition metals. They are simple small and large organic molecules important for excellent selectivity in asymmetric reactions. These compounds are reused, recycled in mechanisms. Organocatalysts are inexpensive, non-toxic and inert towards moisture and oxygen. These are the advantages of organocatalysis over metal catalysis. The current wave of interest in organocatalysis however, is centered on asymmetric catalysis. Even that development is older than most of us recognize as exemplified by Hajos-Parrish reaction using L-Proline for asymmetric aldol condensations. In this write-up we will discuss about the importance of L-Proline as an organocatalyst in a summarized manner.

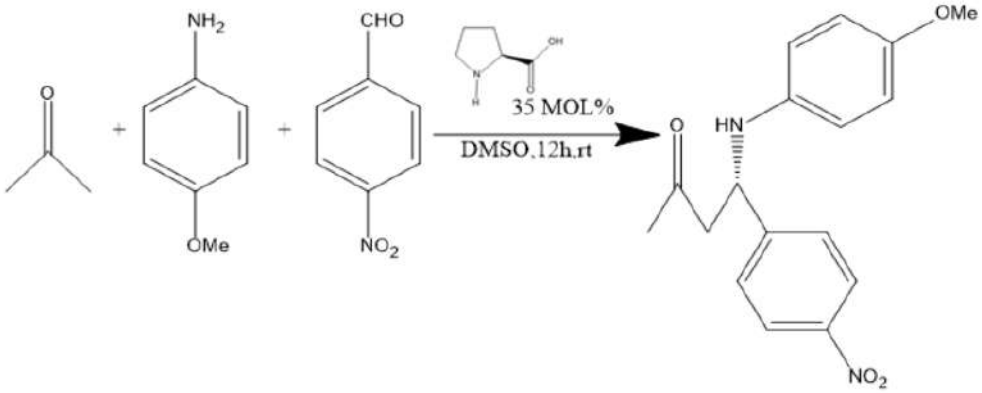
SUMMARY OF THE WORK:

L-Proline is a cyclic, non-essential amino acid in humans, synthesized from glutamic acid and other amino acids. It is found in high concentrations in collagen. L-Proline is pyrrolidine in which the pro-S hydrogen at position 2 is substituted by a carboxylic acid group[1].



L-Proline

B. List and coworkers have reported the first example of the asymmetric Mannich reaction using L- Proline in 2000 and its function as an organocatalyst. The reaction scheme is shown below-

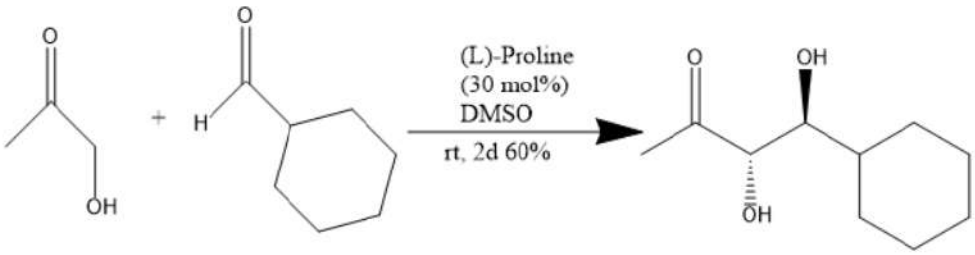


(20 vol%) (1.1eq) (1.0eq) (50% yield, 94% ee)

Scheme-1: Asymmetric Mannich reaction catalyzed by L-Proline

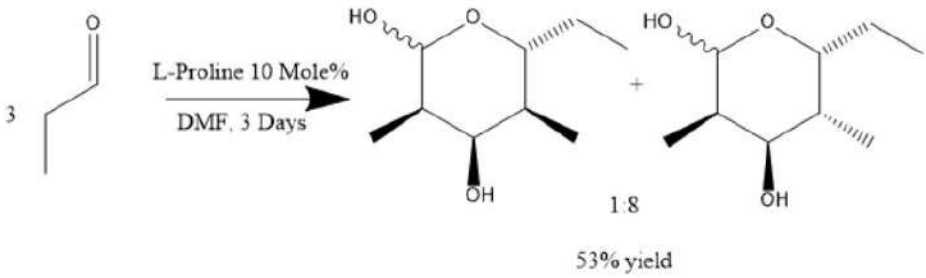
Here acetone (excess), p- nitrobenzaldehyde and p- anisidine are reacted in presence of L-Proline(35 mol%) which gives the product with 50% yield with 94% ee (enantiomeric excess) nature of product [2].

B. List and W. Notz have developed the simple anti 1,2-diol reaction [3].



Scheme-2: Asymmetric Diol Formation

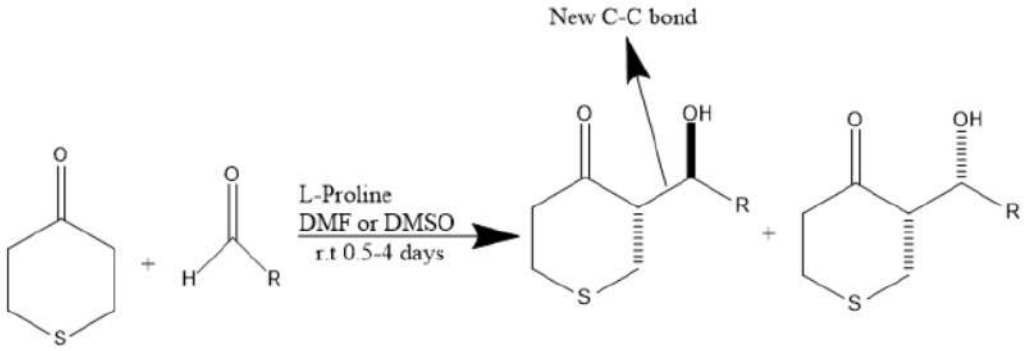
Self aldol condensation reaction catalyzed by L- Proline are also reported.



Scheme-3: Proline- catalyzed self-aldolization reaction of propionaldehyde

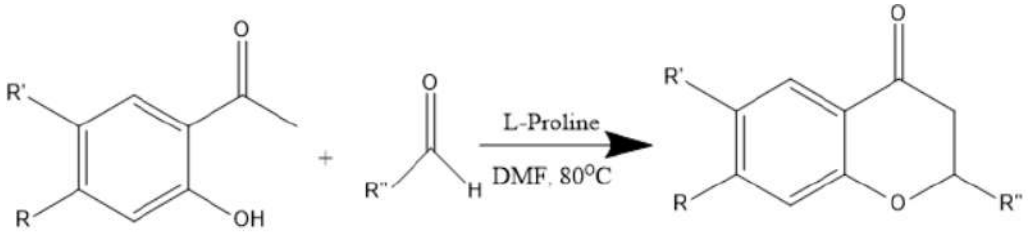
When this reaction is performed with aldolase enzyme, instead of L- Proline then the reaction takes 2 weeks for completion which is a huge time [4].

C-C bond forming reaction could also be performed by using L- Proline as organocatalyst [5].



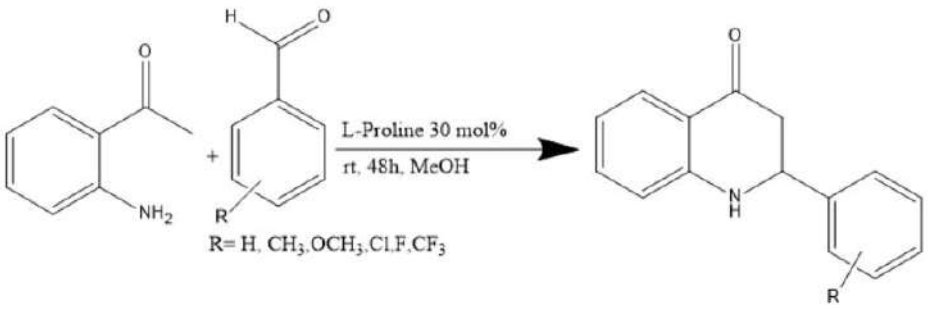
Scheme-4: C-C bond forming reaction using L-Proline

Substituted flavanones are also synthesize by L-Proline as organocatalyst [6].



Scheme-5: Proline catalyzed synthesis of Flavanones

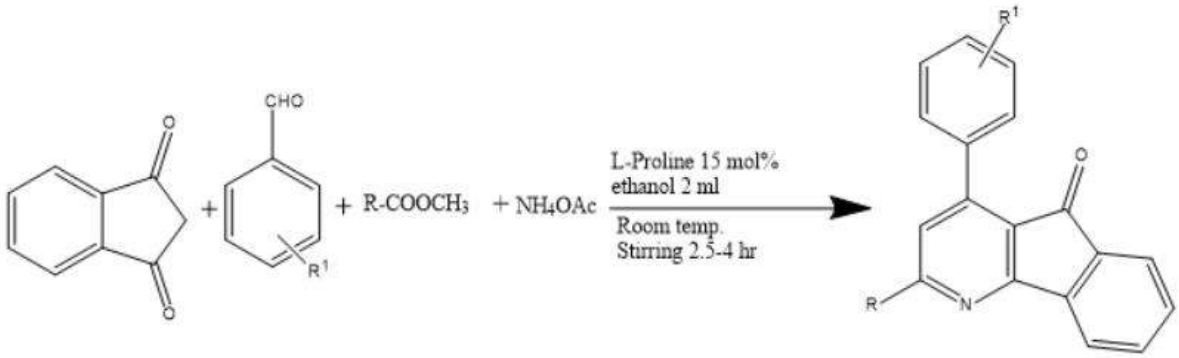
S. Chandrasekhar et al used L- Proline in one-pot synthesis. They synthesize aza- analogue of Flavanones from o-aminoacetophenone.



Scheme-6: Synthesis of aza-analogs of flavanones starting from o-aminoacetophenone

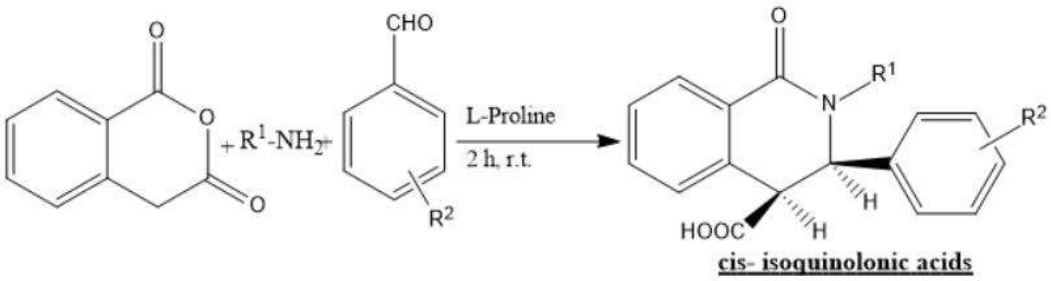
Equimolar quantities of o-aminoacetophenone and benzaldehyde on stirring together in the presence of L-Proline(30 mol%) and methanol as solvent(5ml) and workup furnished 2-phenyl 2,3- dihydroquinoline- 4(1H)- one in 85% yield. In this reaction the organocatalyst L- Proline can be recovered at the end [7].

L- Proline catalyzed multicomponent reactions are also very important. L- Proline gives highly substituted products with excellent yields of pyridine at room temperature. It is inexpensive. Like the below reaction scheme [8].



Scheme-7: Synthesis of highly substituted pyridines by L-Proline organocatalysis

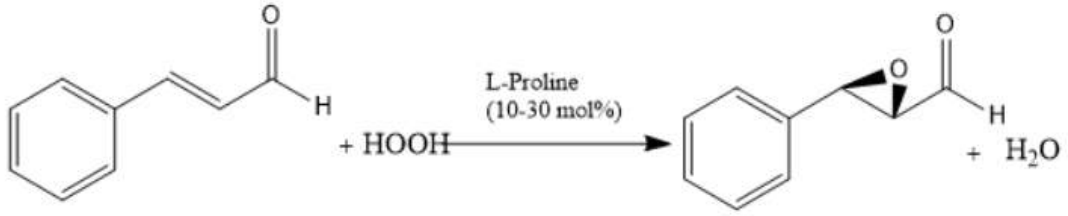
Three component reactions can also give excellent yields in presence of L-Proline as organocatalyst. When aromatic aldehydes, anilines and homophthalic are taken into reaction in the presence of L-Proline (10mol%) as organocatalyst then cis-isoquinolonic acids generates at a very good yield [9].



Scheme-8: Synthesis of cis- isoquinolonic acids

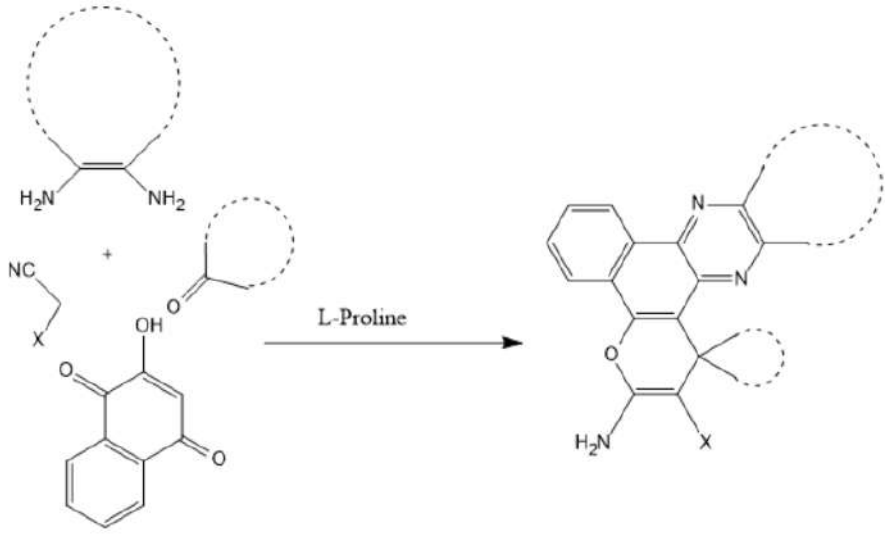
L- Proline can also used in asymmetric epoxidation. When α,β-unsaturated aldehydes react with peroxides or sodium percarbonate in existence of L-Proline which acts as organocatalyst is called asymmetric epoxidation.

Armando Cordova et al explained the probable mechanism, in which α,β-unsaturated aldehydes start activity in presence of L-Proline followed by stereoselective nucleophilic attack conjugatively on the β-carbon which forms a chiral enamine derivative. The process is environment friendly [10].



Scheme-9: Direct catalytic asymmetric epoxidation

Alireza Hasaninejadb and co workers developed a novel method for synthesis of spiro compounds through multi-component reactions catalyzed by L-Proline. In the formed compound the sp3 carbon common between two rings could show biological properties. The yield is very high [11].



Scheme-10: One-pot, four- component synthesis of novel spiro

Conclusions:

In this short write up we discussed some of the organic reactions catalyzed by L-Proline. Many other reactions of L-Proline organocatalysis are also known. This is a still developing field. This field is also important in drug designing. Various derivatives of organocatalysis can also show versatile application in sol-gel process, polyurethanes, L-Proline immobilized nanoparticles, NHC catalysis and Homogeneous and Heterogeneous in asymmetric catalysis. Many derivatives of L-Proline are also used in organocatalysis. So this field has a great importance in organic chemistry. Recently in

2021 **Benjamin List** and **David W.C. Macmillan** has got **Nobel Prize in Chemistry** for their development in ***Asymmetric Organocatalysis.***

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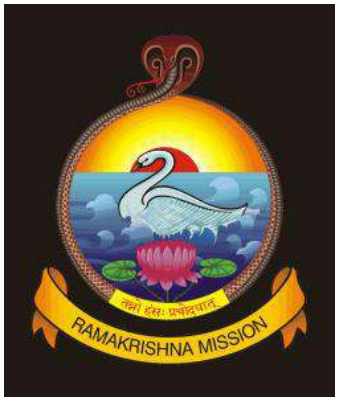
FLUORESCENT CHEMOSENSORS – A ROAD TO SENSING

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

Dwijadas Hati



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FLUORESCENT CHEMOSENSORS – A ROAD TO SENSING

ABSTRACT

Fluorescent chemosensors have been widely applied in many diverse fields such as biology, physiology, pharmacology, and environmental sciences for the detection of biologically and/or environmentally important species. The field of fluorescent chemosensors is being developed for about 150 years. Since then a wide range of chemosensors had been discovered. Despite the progress made in this field, several problems and challenges still exist. This review article provides a general overview of the development in the research of fluorescent sensors. The application of chemosensors in various established and emerging biotechnologies is very bright.

Keywords: Supramolecular Chemistry, Biosensors, Chemosensors, Bioimaging.

INTRODUCTION

Chemosensors are molecular structures that are used for sensing an analyte. When it binds with a specific ion or molecule it produces an observable change that signals the presence of that particular ion or molecule. Fluorescent chemosensors are consisted with a fluorophore part and a binding site. If the binding sites operate via irreversible chemical reactions then the indicators are described as fluorescent chemodosimeters.

The first fluorescent chemosensor was reported by F. Goppelsro¨der in 1867. It was used for the determination of aluminum ion (Al^{3+}) through the formation of a strongly fluorescent morin chelate. Since then a number of fluorescent chemosensors have been developed for the determination of many other metal ions. In this short review we are going to present the subsequent development of chemosensors and their uses in various biological and analytical processes.

At the very beginning, chemosensors were used to detect only metal cation rather than anions and neutral species. This is because these compounds can easily bind metal ions in water. Around 1980, de Silva and Czarnik who are regarded as two fathers of modern chemosensors, pioneered the growth in the development of fluorescent chemosensors. Since those pioneering days, an extensive development of fluorescent chemosensors as well as the scope of their applicability in numerous biological fields, have been extended.

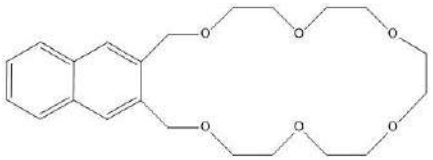
National status: In the last decade huge development has been done by the Indian scientist in the field of chemosensors. Detection of toxic metal ions or bio-molecules is one of the most challenging research fields today. Prof. K. Ghosh and his co-workers designed and synthesized new type of chemosensors for sensing of cations, anions, neutral molecules. Prof. Moorthy and co-workers have significant contribution in the field of supramolecular chemistry and published huge number of research work in the international journel. Prof. Ramanathan and his co-workers performed various research works on the development of fluorescence probes for binding specifically different biological molecules. Prof. N. Parveen and co-workers also carried out evolutionary work in the field of fluorescence imaging using water soluble small molecules. Prof. Chowdhury and his co-workers have significant contribution in the field of Single fluorescence Sensor in solid state using polymer–thin film. The dignified work on the field of fluorescence sensing of biophysically relevant analysis has been improved by of Prof. A. Dutta and his co-workers. Prof. R. Anand and co-workers have also sincere work in the field of biosensors for detecting organic pollutants and process for producing the same. Prof. T. Majumdar and his co-workers have done extensive research work on the field spectroscopic and computational studies of some optical sensors of metal ion and anion. Prof. A. K. Mahapatra and his co-workers carried out versatile research work on the field of Chemosensors, Chemodosimeter and Supramolecular chemistry. This group developed novel small molecules for sensing of metals ions in solution phase.

DISCUSSION

Fluorescent chemosensors for cations: Human body and the environment contains large number of metal ions among them some are essential for our life such as sodium (Na^+) potassium (K^+), calcium (Ca^{2+}), copper (Cu^+ and Cu^{2+}) and zinc (Zn^{2+}) and some are toxic and hazardous such as lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}). To detect these metal ions selectively, a number of chemosensors have been developed.

Fluorescent chemosensors for alkali and alkaline earth metal ions: The mechanism of binding of metals by fluorescent chemosensors involves coordination interactions between the hosts and the guest .Two naphthalene based chemosensors are shown in (Fig 1) i.e. **1** and **2** which also exhibit dichotomous behaviour. It was observed that when 1 formed a complex with alkali metal chloride salts in 95% ethanol glass at 77 K it displayed a decrease in fluorescence quantum yield, also an increase in phosphorescence quantum yield, and a slight decrease in phosphorescence lifetime but for the complexation of **2** with potassium (K^+), rubidium (Rb^+),

or caesium (Cs^+) chloride salts caused a noticeable increase in fluorescence quantum yield, also a decrease in phosphorescence quantum yield, and a substantial decrease in phosphorescence lifetime. The reason behind these changes are the heavy atom effect (for Rb^+ and Cs^+), complexation induced change in triplet energy relative to the ground and excited singlet state energies as well as rigidification and conformational effects.



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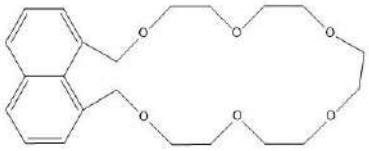

2

Fig.1: Structures of the fluorescent chemosensors **1, 2**.

Fluorescent chemosensors for d-block metal ions:

The uses of chemosensors is not only limited for the detection of alkali metal and alkaline earth metal ions but also they are used to capture the transition metals since these metals take part in various chemical reactions.

Copper (Cu), the third most abundant transition metal in the human body, is involved in various physiological and pathological processes. Imbalance of copper causes diseases like Menkes (copper deficiency), Wilson's (copper overload), Alzheimer's disease, prion disorders, neurodegeneration and cancer.

In 1997, Czarnik and co-workers developed a rhodamine-B derivative and its ring-opening reaction for sensing copper ion (Cu^{2+}).

Fluorescent chemosensors for anions:

Anions play an important role in biological and industrial processes also the environment contains a number of anionic pollutants. There are a number of fluorescent chemosensors have been developed for the detection of anions have used host–guest interactions or chemical reactions, over the past several decades. The mechanism through which they bind with ions may be a guest host interaction or may be a chemical reaction.

Fluorescent chemosensors for small neutral molecules: We have various neutral molecules in environment .While small neutral molecules such as reactive sulfur species (RSS) and some

neutral ROS/RNS are essential for our survival, some small neutral molecules like nitroaromatics (explosives), and nerve-gas are a threat to health. These two important reasons have stimulated the development of fluorescent chemosensors for small neutral molecules over recent years.

Fluorescent chemosensors for reactive sulfur species (RSS): Intracellular thiols such as cysteine (Cys), homocysteine (Hcy) and glutathione (GSH) have vital roles in biological systems. Abnormal levels of these molecules can cause a number of diseases, such as liver damage, leucocyte loss, psoriasis, cancer and AIDS. That is why the detection of these thiolcontaining biomolecules in biological samples has become very important. The first use of PET sensors for thiols was demonstrated by de Silva in 1998. In 2004, two squaraine based fluorescent chemosensors 33a and 33b (Fig.2) was developed for the detection of thiols by Martı´nez-Ma´n˜ez and co-workers. Due to the selective addition of thiols to the cyclobutene ring in the chemosensors these solutions showed colour changes from blue to colorless in the presence of thiol-containing compounds. These thiol chemosensors cannot distinguish Cys/Hcy and GSH.

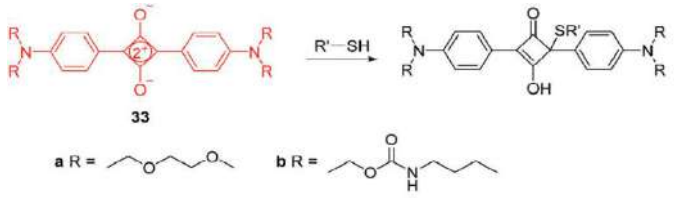

Fig. 2: Structures and proposed mechanism of **33 (a)** and **(b)** for detection of thiols.

Fluorescent chemosensors for biomacromolecules:

In living biological systems biomacromolecules play a vital role. However, the abnormal function of these biomacromolecules often has huge impact on living bodies. The fluorescence imaging techniques is a powerful tool for studying these biomacromolecules and to fully understand their purpose in these complex biological systems. The chemosensors show excellent spatial and temporal resolution and high molecular specificity with these biomolecules. The detection of biomacromolecules is not an easy task as they often have large molecular weights, complex structures and a range of biological functions. Over the past several decades, a number of fluorescent chemosensors have been developed, which have proven to be a must for bioimaging and used in the investigation of diseases.

Czarnik carried out pioneering work on anthrylpolyamine based chemosensors to sense polyanions such as heparin, poly-L-glutamate, ds DNA (double-stranded DNA) and ss DNA (single-stranded DNA) in water. These chemosensors display a redshift and a decrease in their emission spectra when they bound to either ds DNA or to ss DNA.

A pyrene-based peptide beacon (fluorescent chemosensor 46) has been reported by Schmuck and co-workers. It was shown to intercalate with DNA (Fig.3). While the folded conformation of 46 exhibits a typical pyrene excimer emission in solution, it undergoes a conformational change to the unfolded form when bound to DNA. During the change in conformation, a ratiometric change in fluorescence from excimer (490 nm) to monomer emission (406 nm) is observed.

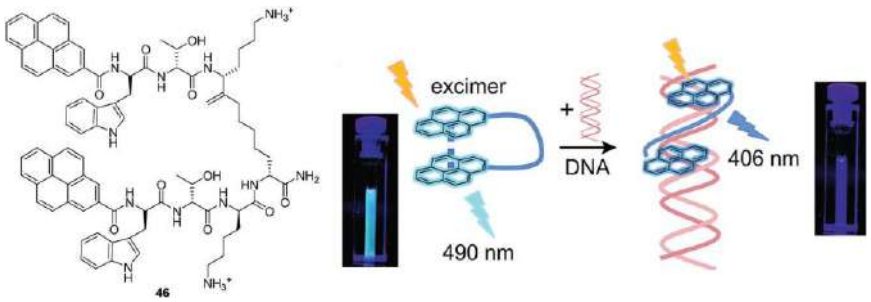

Fig.3: Structures of the fluorescent chemosensors **46** and the schematic illustration of **46** and Its Interaction with nucleic acid (the photographs show the corresponding cuvettes under UV light).

CONCLUSION

Over the past 50 years the field of fluorescent chemosensors has been developed explosively. The growth in this vast field is deeply pioneered by the research of Professor Anthony W. Czarnik's and Professor A. Prasanna de Silva. Within a very short time the field is flourished and is recognised as a branch of chemistry. Research workers expect that the field of chemosensors will continue to expand. To meet new challenges we need increasing number of new and improved chemosensors as well as we have to find new approaches or applications of existing fluorophores.

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WASTE TO ENERGY STATUS IN INDIA

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. Supratim suin

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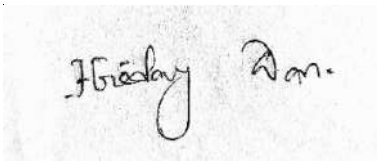

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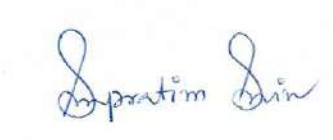
Date:- 28-01-2022

Certified that the short review entitled “WASTE TO ENERGY STATUS IN INDIA” submitted by **Mr. Hriday Das** [Registration No.: A01-1122-112-036-2019] for the partial fulfillment for the B.Sc. degree in chemistry in Ramakrishna Mission Vivekananda Centenary College, Rahara has been executed under my guidance.



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ABSTRACT

India is one of the most rapidly developing countries in the world. It is witnessing growing industrialization and thus development. Such rapid development needs energy to process, which further makes India an energy hungry nation. Current India depends mainly upon fossil fuels and thus has to pay a huge bill at the end of every contractual period. These bill can be shortened and the expenditures brought down by using and exploiting non-conventional sources of energy. India holds a huge potential for such non-conventional sources of energy. A population of 1.2 billion generating 0.5 kg waste per person every day. Thus, sums up to huge pile of waste, which is mostly landfilled in the most unhygienic manner possible. Such unmanaged waste not only eats up resources but demands expenditure as well. This can lead to the downfall of economy and degradation of the nation. Thus, this short review investigates the waste to energy strategies as a solution to both the problems stated above. The strategies will not only reduce the amount of waste, but also produce energy from the same, thus achieving waste management as well as energy security.

Keywords: Waste management, waste to energy, non-conventional energy

1. Introduction

Waste-to-energy (WtE) or energy-from-waste is the process of generating energy in the form of electricity and/or heat from the primary treatment of waste, or the processing of waste into a fuel source. WtE is a form of energy recovery India, the 11th largest economy in the world in terms of Gross Domestic Product (GDP) and the 3rd largest economy in the world in terms of Purchasing Power Parity (PPP), is a fast developing nation [1]. India, the second most population of 1.3 billion, has witnessed a population growth of 31.8% during the last decade [2].

The rapid increase in population witnessed by the country puts a strong declining thrust on the nation's resources. The 3Rs (Reduce, Reuse and Recycle) should be kept in mind while working towards resource utilization. On the contrary if optimum resource utilization is not supervised upon, it can lead to an increase in waste, pollution and a down fall in the economy, but also take a toll on the environment and the health of the citizens through harmful emissions. Thus it is of utmost importance to keep a constant eye on utilization and recovery of resources. Changing life style and fashion over the years has led to a huge change in the amount of waste generated [3]. The most common practice of managing waste today is landfilling, which poses a huge threat to the environment in the form of green –house gases (GHG) leakage in the form of CO_2 and CH_4 and leachate production thus this technique needs to be improved [4]. Thus, there is an urgent need to come up with an environmentally, economically and socially sustainable solid waste management process. Waste to energy is one such process that has long been neglected, but holds strong potential to derive energy from the unused resource, i.e., waste.

2. Types of waste management practices

The waste management practices are not able to cope up with the rate at which the waste is generated. This has attracted the attention of many, and thus, the field of waste management has witnessed many innovation. Various type of waste conversion process are available. The waste conversion processes commonly in use are thermal conversion (incineration, pyrolysis, gasification, refuse derived fuel (RDF)), bio-chemical conversions (composting, vermicomposting, anaerobic digestion/biomethanation) and chemical

conversions (trans-esterification and other processes to convert plant and vegetable oils to biodiesel).Each of them has their corresponding advantage and limitation. In this section we are learn about them.

2.1. Incineration

Incineration, the combustion of organic material such as waste with energy recovery, is the most common WtE implementation. All new WtE plants in OECD countries incinerating waste must meet strict emission standards, including those on nitrogen oxides (NOx), sulphur dioxide SO_2, heavy metals and dioxins [8]. Hence, modern incineration plants are vastly different from old types, some of which neither recovered energy nor materials. Modern incinerators reduce the volume of the original waste by 95-96 percent, depending upon composition and degree of recovery of materials such as metals from the ash for recycling [10].

Incinerators may emit fine particular, heavy metals, trace dioxin and acid gas, even though these emission are relatively low [11]from modern incinerators. Other concerns include proper management of residues: toxic fly ash,which must be handle in hazardous waste disposal installation as well as incinerators bottom ash (IBA), which must be reused properly [12]. The method of incineration to covert municipal solid waste (MSW) is a relatively old method of WtE generation. Incineration generally in tails burning waste (residual MSW, commercial, industrial and RDF) to boil water which powers steam generators that generate electronic energy and heat to be used in homes, businesses, institutions and industries. One problem associated in the potential for pollutants to enter the atmosphere with the flue gases from the boiler. These pollutants can be acidic and in the 1980s were reported to cause environmental degradation by turning rain into acid rain. Modern incinerators incorporate carefully engineered primary and secondary burn chambers, and controlled burners designed to burn completely with the lowest possible emission, elimination, in some cases, the need for lime scrubbers and electro-static precipitators on smoke stacks. New York Time, modern incineration plants are so clean that ‘many time more dioxin is now released from home fireplaces and backyard bar because than from incineration. [13]. Compared with other waste to energy technologies,

incineration seems to be the most attractive due to its higher power production efficiency, lower investment cost, and lower emission rate.

2.2. Fuel from plastics:-

It aims to solve major environmental issues namely pollution caused due to plastic waste accumulation and the need for an alternative fuel source. The process that is used to convert plastic into fuel is pyrolysis .It is the thermal decomposition of materials at very high temperature in an inert atmosphere. It involves change of chemical composition and is mainly used for treatment of organic materials, In large scale production ,plastic waste is ground and sent for melt feeding and then the process of pyrolysis takes place, catalytic converters helps in the process and the molecular rearrangement of polymers takes place, the vapors are condensed with oil or fuel and accumulated in setting tanks and filtrated, fuel is obtained after homogenation and can be used for automobiles and machinery, It is commonly termed as thermo-fuel or energy from plastic[14].

2.3. Biochemical conversion

Biochemical conversion of waste to energy is much more eco- friendly. Biochemical conversion primarily consists of converting the waste into energy by the action of enzymes of microorganisms. The techniques falling under this category are anaerobic digestion and composting. In Anaerobic digestion (AD), organic waste is fed to the process as feedstock, which is acted upon by microorganisms in absence of oxygen. This reduces the amount of waste and produces.

3. Worldwide status of waste to energy (WTE)

During the 2001-2007 period, the waste-to-energy capacity increased by about four million metric tons per years Japan and China each built several plants based on direct smelting or on fluidized bed combustion of solid waste. Japan is the largest user in thermal treatment of municipal solid waste in the world, with 40 million tons. Some of the newest plants use stoker technology and others use the advanced oxygen enrichment technology. As of June 2014, Indonesia had a total of 93.5 MW installed capacity of waste-to-energy, with a

pipeline of projects in different preparation phases together amounting to another 372MW of capacity. [15]

The developed countries have started implementing it successfully as measured of west management as well as energy security. Increasing development leads to a change in lifestyles and status, leading to a burgeoning amount of waste generation. Thus, many countries have taken a step forward and started recovering energy from garbage. In USA in 1990, an estimated 394 trillion Btu of energy was consumed, produced from MSW. According to Japanese Ministry of Health and Welfare (MHW), electricity generation was in operation at 102 waste incineration plants as of late 1991.

Many waste-to-energy plants ware operational in Germany in the 90's. Cleaner fuels and modern incineration technology resulted in 90% reduction in Swedish incineration plant emissions since 1985. United Kingdom, the 70th report by the Royal Commission on Environmental Pollution very precisely stated the importance of modern technology in the field of waste to energy [5].

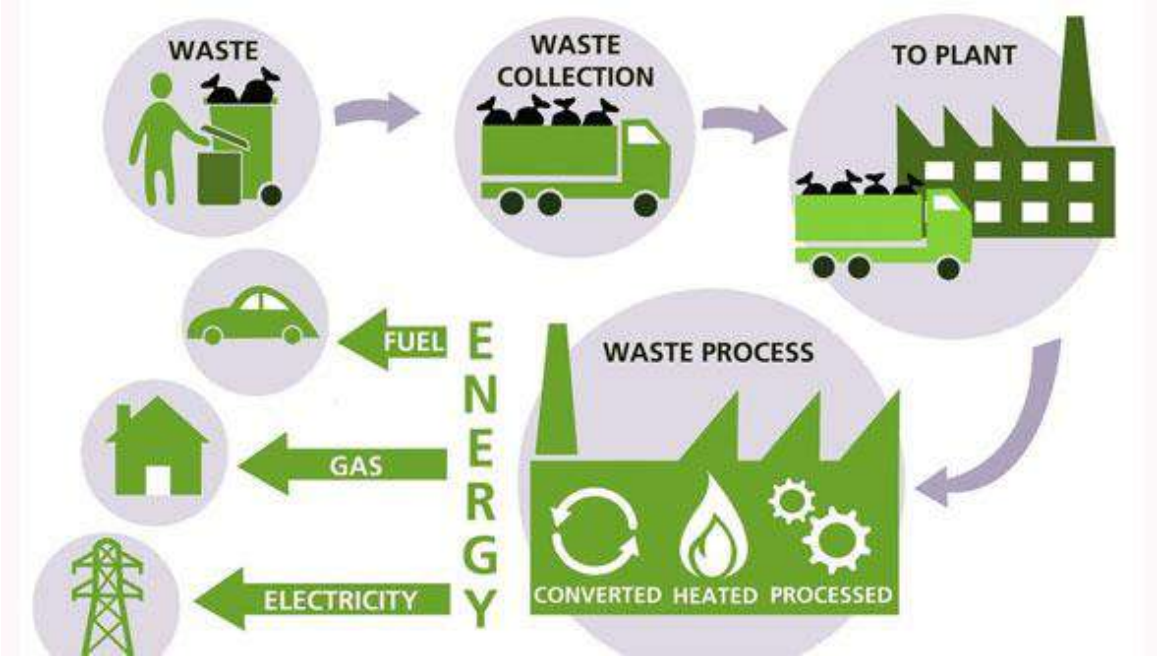

Figure 1: *Representative waste to energy process.*

[Ref: https://engmag.in/waste-to-energy-may-not-brilliant-idea-yet/]

Let us have a look at the current practices of waste to energy, globally. Poland uses agricultural biomass to generate electricity .At the end of 2012, there were 29 agricultural biogas plants in the Poland with an average installed capacity of 1 MW [6]. Italy has witnessed installation of many anaerobic co-digestion plants ranging between 50 kW and 1MW [7]. Agricultural biomass has been used as feedstock in many African countries including Ghana to produce decentralized rural energy. The total output they obtain is 12.5kw electric powder using two generators rated 5kVA and 7.5 kVA. The produce electricity is supplied to the community using a local grid of 230 V for 12 h per day [8]. Singapore has been long focusing on the energy recovery option from food waste produced and thus has formulated many policies to promote the same [9]. Thus the time is ripe for the developing as well as under developed nations to start emulating these nations and take a step forward in the direction of sustainable MSW management practice.

4. Waste to energy status in India

4.1. Waste generation in India

Changing lifestyles and increasing PPP of urban Indians, has increased the per capita waste generation rate in India from 0.44kg/day in 2001 to 0.5kg/day in 2011.India has 53 cities with a million plus population, which together account for 86,000 TPD (31.5 million tons per year) of waste generated .The total Municipal Solid Waste (MSW) generated in India is estimated 68.8 MTY or188500 TPD [2]. So this huge amount of generated waste in India not only effect the nature of India but also effect the threat to health .So we must to proceed forward to minimize the amount of waste generated in India.

4.2. State wise waste to energy status

India is a developing country and thus produces a huge amount of waste every year. Recovering energy out of the waste produced is a complicated, yet, resourceful method. India has always been lagging in this field owing to reasons namely the lack of policy framework, technological advancements, infrastructure, sustainable planning and insufficient funding sources [18]. Let us have a lock at the various wastes to energy projects operating throughout the country in a state-wise manner.

4.2.1. Delhi

The first large scale waste incineration plant was set up at Timarpur, New Dekhi in 1987, by Miljotecknik Volunteer, Denmark. It has a capacity of 300t per day and costed INR 250 million. The plant was out of operation within 6 months which forced Municipal Corporation of Delhi to shut it down .The latest development in the same direction is the setup of another incineration plant at Okhla land fill site, New Delhi, which has designed to generate 16 MW of electricity by combusting 1350 t per day of MSW. ln addition, a gasification unit is also installed at Gaul Pahari campus, New Delhi, by the Energy Research Institute(TERI)[19].

4.2.2. Rajasthan

A gasifier unit has been installed at nohar, hanungarh by the narvreet energy Reserch and information (NERI) combust forest wests, agro-wastes and saw mill dust. With an efficiency of 70%-80%, the waste feeding rate is about 50-150 kg/h out of the total fuel gas produced, about 25% is recycled back into the system to support the process, while the remaining fraction is recover and used for power generation [20].Apart from this, a RDF plant is installed near Jaipur. It combusts the RDF produced in cement kilns to replace fossil fuels and handles 500 TPD of waste. It is not operated regularly [2].

4.2.3. West Bengal

According to a study conducted by [21],waste to energy does not appear to be feasible as a waste reduction process ; at either large scale or small scale .thus ,currently waste to energy process is not considered as a MSW management at West Bengal is due to lack of waste segregation at source ,low percentage of waste segregation at source, low percentage of house to house collection, large number of open vats, low operational efficiency of waste transport system with old vehicles ,low collection efficiency in newly added areas and an inefficient informal recycling system .after repeated experimentation and research, West Bengal is looking forward to attract investors in this field. Many other states in India are very aggressive in this field. However, this is data in few states improvement of waste to energy techniques.

4.3. Failure of Waste to energy projects in India

India is a developing country and thus is witnessing a rapid rise in the amount of waste it generates every day, month and year .Ten aerobic composting projects in 1970s, a WTE project in 1980, a large scale bio methanation project, and two RDF project in 2003, have all met with failure. Large scale bio methanation has failed owing to the absence of source separation .A major plant in Lucknow to produce 6MW electricity failed due to this reason .However the same process has shown hungry success on small scale, using kitchen waste market waste, restaurant waste, etc. India has a total of 5RDF processing plants, all of which have encountered operational problems due to lack of proper financial and logistical planning and not due to technology, .RDF plant have already been shut down [2]. The initial failure of waste to energy technologies to make the people against this techniques but this is the key barrier of development today. Though the process many people attract to this technologies.

5. Difficulties and Recommendations

Waste to energy process has been long tried at various Indian cities, but has generally met with failures when compared with the other nations. The main causes behind these failures are lack of financial and logical planning and absence of strong policy framework for waste to energy process, a number of initial failures over the decades have turned the citizen as well as investors against the process. Also the increasing prices of fuel and power have made such waste to energy project much more viable. Thus many investment in the form pilot as well as large scale plants have been witnessed throughout the nation. Here, I propose some recommendations, which are believed to resolve the issue.

A. There is need for micro or locality base plants which can provide details as to routes, timing equipment and manpower development for achieving a high level target collection transportation, treatment and disposal.

B. Primary collection i.e. door to door collection and segregation at house hold level on regular basis may give a new lease of life to the existing MSWM system in India.

C. Proper source segregation of wastes. This step is necessary to isolate the wastes according to their merit.

D. Proper infrastructural facilities and training to street sweepers etc.

E. Development of dedicated R & Ds to manage wastes and transform them into energy. Industry academia collaboration can led to good results in this aspect.

5. Conclusion

In this short review we have tried to give some lights on the solid waste management and its utilization in energy generation. The conventional procedures of waste management, waste to energy status in India and Worldwide have briefly been discussed. As can be seen, India has faced several problems in Waste to Energy drive while the large economies worldwide have do well in this aspect. Proper planning, strong willpower of Govt. as well as people, research and developments in the field of Waste to Energy are expected to result in grand success in both the waste management and energy generation.

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METHODS OF DETERMINATION OF AMINO ACID SEQUENCES IN PEPTIDES

Project work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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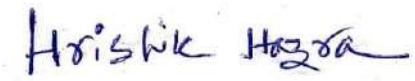

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METHODS OF DETERMINATION OF AMINO ACID SEQUENCES IN PEPTIDES

ABSTRACT:

In 1950 Edman published a chemical method for the stepwise removal of amino acids from the N-terminus of a peptide.[1] This series of reactions has come to be known as the Edman Degradation, and although modifications of this technique have been introduced from time to time, Edman Degradation remains, thirty years after its introduction, the only effective chemical means of removing amino acids in a stepwise fashion from a polypeptide chain.

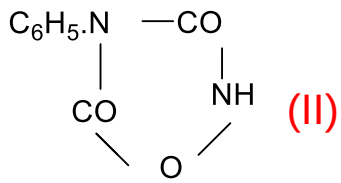
INTRODUCTION:

The determination of amino acid sequences in a peptide has drawn the interest of several investigators in the past because of biological interest. This subject has been studied by Fox, since the new approaches like partial hydrolysis, have been made by Consden, Gordon, Marti and Synge.

The applicable methods suffer from some restrictions and hence search for alternative methods become a challenge to the chemists.

In 1927 Bergmann, Kann and Miekely described the following reaction:

(I) $C_6H_5.NH.CO.NH.CHR'.CO.NH.CHR''.COOH \rightarrow$



(II)

$H_2N.CHR''.COOH$

RESULTS & DISCUSSION / SUMMARY OF THE WORK:

Refluxing with hydrochloric acid split off the phenyl hydantion(II) from the phenylcarbamyl peptide (I). The fact that the resistance to acid cleavage was less than that expected for a peptide bond, indicating a labilizing effect of the phenylcarbamyl group, apparently escaped the authors' notice. Later Abderhalden and Brockmann took advantage of this effect in developing a method for the stepwise degradation of polypeptides. Concomittantly, however, to the desired cleavage other peptide bonds in the chain were also attacked to some extent. This circumstance obviously detracts from the usefulness of the procedure.

The present attempt to employ the above reaction for the determination of peptide structure was guided by several considerations. Firstly, it was postulated that the ease of the reaction parallels the ease of ring closure to hydantoin and from that point of view the phenylthiocarbamyl derivatives should be preferable.

Secondly, the cleavage should take place exclusively at the peptide bond adjacent to the carbamyl group, other bonds remaining untouched. Since the hydantoin formation does not require the presence of water, whereas of course peptide linkages are split by hydrolysis or analogous reaction, it was decided to carry out the reaction in an anhydrous, inert solvent. It was found that nitromethane was ideal in this respect. Nitromethane saturated with hydrogen chloride brought about an almost instantaneous and quantitative cleavage of phenylthiocarbamyl (PTC) dipeptides into phenyl thiohydantoin and amino acid at room temperature. It could also be shown for a PTC-tripeptide that the cleavage took place exclusively at the peptide bond adjacent to the PTC-substituent.

The first part of the experimental section describes the formation and mode of cleavage of some PTC-peptides and the second part deals with the application of these reactions in a procedure for stepwise degradation of polypeptides on a micro scale.

1. Preparation and cleavage of phenylthiocarbamyl (PTC) peptides

Nitrogen determinations were made by the micro-Kjelduhl procedure. Melting points were determined on a heating block (Fidor-Jobns) and are uncorrected, Prior to analysis the preparations were dried for 4 hours in a vacuo (1 mm Hg) over p_{2O5}, and pellets of KOH

Preparation and cleavage of PTC alanylglycine: DL-alanylglycine (0.20 g) was dissolved in 10 ml pyridine-water (1:1). The solution was warmed to 40 ^{o}C and 1 N NaOH was added to make pH 6 (glass electrode) which was maintained throughout the reaction by the addition in small portions of N NaOH. To this reaction mixture 0.48 ml phenyl isothiocyanate was added with vigorous stirring. The reaction was complete within half an hour. The total amount of N NaOH added was 2.4 ml. Pyridine and excess phenyl isothiocyanate were removed by repeated extractions with equal volumes of benzene. On the addition of N HCI to pH 3 phenylthiocarbamyl-alanylglycine separated as an oil which solidified on standing over night in the ice-box. Yield 0.44 g. The material was then recrystallized from ethanol-water. M. p. 155.

Found: N, 15.00. $C_{12}H_{15}O_3N_3S$ requires N, 14.95.

PTC-alanylglycine (0.28 g) was dissolved in 20 ml anhydrous nitromethane saturated with hydrogen chloride. Glycine.HCl started to crystallize out immediately and was filtered off after 15 minutes. Yield 89%. The material was then recrystallized from ethanol-water. Found: N, 18.95. Calc: 18.60; paper chromatography using pyridine-amyl alcohol showed identity with glycine.

The nitromethane solution was evaporated to dryness at reduced pressure. The residue was taken up in a small volume of hot glacial acetic acid and a minor, insoluble residue filtered off. On addition of water to the glacial acetic acid solution and cooling a solid separates out. The material was recrystallized from ethanol. M. p. 184-85. Mixed m.p. with an authentic sample of 5-methyl-3-phenyl-2-thiohydantoin m.p 185 ^{o}C.

Preparation and cleavage of PTC-leucylglycine: L-leucylglyine (0.38 g) was treated as described for PTC-alanylglycine. The yield of phenylthiocarbamoyl-leucylglycine was 0.32 g. The material was then recrystallized from ethanol-water. M. p. 147-48.

Found: N. 13.07. $C_{15}H_{21}O_3N_3S$ requires N, 13.01.

PTC-leucylglycine (0.34 g) was dissolved in 20 ml nitromethane-HCl, glycine hydrochloride immediately started to separate and was filtered off after 15 minutes. Yield 93 %; It was then recrystallized from ethanol-water. Found: N. 18.87. Calc: 18.06. Paper chromatography using pyridine-amyl alcohol demonstrated identity with glycine.

The nitromethane solution was evaporated is vacuo to dryness and the residue extracted with a small volume of hot glacial acetic acid. On addition of water and cooling in the ice box crystals appeared, which were recrystallized from ethanol-water. M. p. 177-78 ^{o}C; the mixed m. p. with an authentic sample of isobutyl-3-phenyl-2-thiohydantoin" was 178 ^{o}C.

Preparation and cleavage of PTC-leucyltyrosine: L-leucyl-L-tyrosine (0.60 g) was treated as described for DL-alanylglycine. The yield of phenylthiocarbamoyl-leucyltyrorine was 0.72 g. It was then recrystallized from ethanol-water M. p. 225-30 ^{o}C with decomposition. Found N, 9.00. requires N. 9.78

PTC-leucyltyrsine (0.43 g) was dissolved in 20 ml nitromethane-HCl. Crystallization of tyrosine hydrochloride started immediately. The crystals were filtered off after 15 minutes. Yield 98 % Recrystallisation was carried out by dissolving the crystals in the smallest possible volume of water and neutralizing with sodium hydroxide. Found: N. 7.68. Calc, 7.12. Paper chromatography using pyridine-amyl alcohol showed identity with tyrosine.

The nitromethane solution was evaporated in vacuo to dryness and the residue extracted with a small volume of hot glacial acetic acid. Crystallization occurred on addition of water and cooling in the ice box. The material was then recrystallized from ethanol water. M. p. 176-77 ^{o}C. The mixed m. p. with an authentic sample of 5-isobutyl-3-phenyl-2-thichydantoin was 176-77 ^{o}C.

Preparation and cleavage of PTC-glycyltryptophan: Glycyl-L-tryptophan (0.52 g) was treated as described for DL-alanylglycine. The yield of phenyl thiocarbamyl-glycyltryptophan was 0.71 g. Attempts to crystallize from organic solvent yielded only oils. The reaction mixture was then dissolved in the minimum amount of 0.5 N NaOH from which a solid crystallized out on the gradual addition of N. HCL. M. p. 120-23 ^{o}C.

Found: N. 13.75, $C_{20}H_{20}O_3N_4S$ requires N, 14.14.

PTC-glycytryptophan (0.40 g) was dissolved in 20 ml nitromethane-HCl. Tryptophan hydrochloride began to crystallize out within a few seconds. After 15 minutes the crystals were filtered off. Yield 98%; it was then recrystallized from ethanol-water. Found: N, 13.3. Calc: 12.71. Paper chromatography using pyridine-amyl alcohol showed identity with tryptophan,

The nitromethane solution was evaporated to dryness in vacuum. The dark, brown residue was taken up in a small volume of hot ethanol and an insoluble residue filtered off. Addition of water to the alcoholic solution brought about precipitation. The material was recrystallized from ethanol. A brownish impurity was, however, very difficult to separate from the reaction mixture. The crystals were then sublimed and resublimed at 150 in a vacuum of 0.05 mm Hg which resulted in a slightly yellowish product. M. p. 340-4 ^{o}C with decomposition. An authentic sample of 3-phenyl-2-thiohydantoin melted at 245-48 ^{o}C with decomposition. Found N, 14.40. Calc: for $C_9H_8ON_2S$: N, 14.58.

Preparation and cleavage of PTC-alanylleucylglycinL: DL-alanyl-L-leucylglycine (0.13 g) was treated as described for DL-alanylglycine except that only half the amounts of reagents were mand. The yield of phenylthiocarbamoylalanylleucylglycine was 0.16 g. The system resisted all attempts of crystallisation. It was purified through repeated precipitations with water from its solution in glacial acetic acid. Found: N, 12.00. $C_{18}H_{26}O_4N_4S$ requires N, 14.22.

PTC-alanylleucylglycine (40 mg) was suspended under anhydrous conditions in 2 ml nitromethane-HCI at 40 ^{o}C by means of a magnetic stirring device. After 15 minutes nitromethane and hydrogen chloride were removed by careful evaporation in vacuum at room temperature. To the dry residue were added with stirring 1 ml of water and then dilute NaOH to pH 9. The solation was again evaporated to near dryness in vacuo at room temperature. The residue was extracted with glacial acetic acid and of this solution aliquote were taken for determination of total nitrogen and amino nitrogen according to Van Slyke with the modifications introduced by Kendrick and Hanke Found: N. 5.50 mg.; amino-N, 1.35 mg: amino-N/total N, 0.246. The calculated quotient for the cleavage of one peptide bond in 0.25 making the actual cleavage 98 % of the calculated. PTC-alanylleucylglycine (40 mg) was treated with 2 ml nitromethane-HCI as described in the preceding section. After the removal of nitromethane and hydrogen chloride the residue was thoroughly extracted. Paper chromatography using pyridine-amyl alcohol was performed on the aqueous solution. 0.02 ml of

the solution was applied to the paper alongside authentic samples of leucylglycine, leucine and glycine. From the test sample was obtained only one spot with the same R-value as that of leucylglycine and no trace of leucine (R, 0.58) or glycine (0.19). But the treatment of the PTC-peptide with nitromethane HCI caused a cleavage to 1% of the peptide bond between leucine and glycine, there should have been present 2.5 % of leucine and 1.5 % of glycine in the applied test sample.

Actual experiment showed that it was easily possible to demonstrate the presence of these amounts on a paper chromatogram. Consequently an eventual cleavage of the bond between leucine and glycine must have been less than 1%.

CONCLUSIONS:

The applicability of the method can only be briefly discussed in view the limited number of instances in which it has been employed. It is obvious from the very nature of the procedure that the presence in the peptide of a free alpha amino group is a prequiosite for its applicability. Furthermore only molecules exclusively built up of peptide bonds between α-amino (α -imino) and α -carboxyl groups can be expected to lend themselves to a complete degradation.

It is possible that some of the amino acids will behave differently from those investigated. Of particular interest in this respect are the amino acid serine, threonine and cystine because in these cases there is a tendency for other reactions to occur concomittantly with the hydantoin formation.

It has been shown that optical activity is more or less completely lost on the formation of phenyl thiohydantoins from optically active amino acids. Whether or not racemisation will occur under the different conditions of the degradation procedure is of obvious interest and will be investigated.

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WASTE TO ENERGY: STRATEGIES AND GLOBAL STATUS

A Short Review

Submitted for partial fulfillment of the B. Sc. degree in Chemistry

By

KISHOR BISWAS

[Registration Number-A01-1122-112-038-2019]

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Certificate

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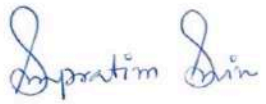
Certified that the short review entitled "WASTE TO ENERGY: STRATEGIES AND GLOBAL STATUS" submitted by **Mr. Kishor Biswas** [Registration No.: A01-1122-112-038-2019] for the partial fulfillment for the B.Sc. degree in chemistry in Ramakrishna Mission Vivekananda Centenary College, Rahara has been executed under my guidance.



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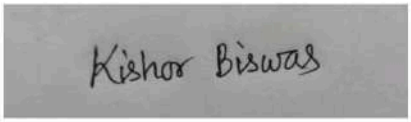

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ABSTRACT

Production of wastes with huge amounts represents a big problem for many countries. Also, transportation and disposal of these amounts are land and resources consumers so managing .These wastes became an urgent issue recently. Waste management includes recycling, safe disposal of hazardous waste materials and using materials which have reasonable calorific value to be converted into energy. Waste to energy concept provide economical and Environmental benefits and introduce a renewable energy source as well. Utilization of wastes as renewable source of energy can achieve environmental sustainability and compensate the shortage of other energy sources. Energy demand and consumption increased dramatically over the previous few years, for example the world daily consumption of natural gas and oil from 261 billion cubic feet and 85.4 million barrels in 2009 to reach about 335 billion cubic feet and 91.2 million barrels in 2013 by an increase of about 28% and 7% of natural gas and oil consumption respectively. Thus, significant research focous has been put worldwide in recent years towards converting wastes into energy which not only resolve the pollution but also fulfill the energy crisis. In this short review, we have tried to find out the waste to energy strategies and status presently active globally.

Keywords: Waste Problems, Energy Demand, Waste to Energy, Environmental Sustainability.

1. INTRODUCTION

1.1. Waste Problem

World countries suffer from the big problem of waste production in huge amounts every year. These wastes have serious impacts on environment and surrounding landscapes. They include Municipal solid waste MSW, industrial wastes, agricultural wastes, etc… On the basis of their State, they could be classified into different types such as solid or semi-solids including Organic, plastic, papers and many other useful or hazardous waste. Agricultural wastes could be leaves, tree cuts, crop residues, husks or roots. Domestic and industrial waste water are the two main sources of semi-solid wastes. Proposed management alternatives for such waste must be considered.

1.2. Waste Management Overview

Solid waste management normally begins with its collection and ending by safe disposal, passing through transportation, segregation and processing. According to the type of the Waste processing is planned. For MSW processing is conducted after segregation to organic, Which may be composted [1], recyclables as glass or plastics which may be recycled [2], and Non recyclables having high calorific value are directed to profitable products known as Refused derived fuel RDF used as alternative fuels for energy consuming industries as cement [3]. Processing and uses of agricultural waste vary between animal feed, fertilizers or energy Sources [4]. Semi-solids and used oil are physically and chemically treated for reuse [5], or being used as renewable energy source through biodiesel production [6].Hazardous and non-recyclable wastes are normally incinerated or landfilled. Examples of these wastes are: radioactive waste materials, medical wastes, wastes from leather tanning Industry, etc. Medical wastes are first incinerated then the remaining ashes are disposed [7].

1.3 Energy Problem and the Need for New Resources.

Energy demand increases steadily due to the yearly increase of population as well as rise of living standard that lead to increase the demand of new energy sources. Over the previous few years, the world daily consumption of natural gas and oil increased from 261 billion cubic feet and 85.4 million barrels in 2009 to reach about 335 billion cubic feet and 91.2 million Barrels in 2013 by an increase of about 28% and 7% of natural gas and oil consumption respectively [8]. By the end of 2015 the daily oil consumption increased by about 4.2% from that of 2013. Based on the above estimation, new and

renewable energy resources should be developed to overcome the problem of fossil fuels shortage over the upcoming decades.

2. WASTE TO ENERGY WTE CONCEPT

The simple definition of waste to energy concept is using different wastes for energy production as alternative energy sources instead of conventional sources. Waste materials with a reasonable calorific value can be used for energy generation directly after simple. Processing as sorting and shredding or through more complicated processes such as thermo-chemical processes like trans-esterification and pyrolysis. It may be observed that products from thermo-chemical processes have higher calorific values due to the elimination of non-combustible content from the waste materials. These products should be upgraded to match the international standards.

2.1. Different WTE Processes

As mentioned before, WTE processes may be classified as direct and indirect ones. Direct processes may be conducted by combustion of RDF, activated sludge, used tires or agro-waste while indirect processes deal with the production of fuel alternatives through other thermo-chemical processes such as trans-esterification, pyrolysis, gasification, digestion, Fermentation, etc...

2.1.1. Direct WTE Processes

One of the good examples of direct WTE processes is the use of RDF for energy production in cement plants. As mentioned before, RDF is the remaining non-recyclable part of MSW and it should be further processed to be used for energy production. RDF should be shredded, screened and dried; the energy content per unit mass of RDF is about one third that of natural gas which make it a promising alternative for fossil fuels [9]. Activated sludge, used tires and Agro-wastes can be used directly to generate energy but using these materials may have some drawbacks such as the emission of Sox and NOx gases when combusted [10] and in the case of using activated sludge it may be harmful because of the presence of heavy metals [11] Agricultural and farm wastes are demanded in other industries, e.g. pulp industry and production of animal feed [12], but this problem can be solved through the optimization between different uses of these valuable wastes.

2.1.2. Indirect WTE Processes

2.1.2.1. Waste oil WO trans-esterification

WO can be converted into biodiesel through transesterification where WO reacts with an alcohol in presence of a catalyst to produce fatty acid alkyl ester, i.e. biodiesel, and glycerol as a valuable by product [13]. The most applied method is the homogeneous base catalyzed trans-esterification where alkaline base catalyst such as potassium hydroxide KOH, is used [14]. If the free fatty acid content is higher than 2% of WO weight, an esterification step should be performed using an alcohol in high excess in presence of mineral acid as a catalyst to decrease the free fatty acids content to make WO suitable for the trans-esterification step [15]. After reaction, different phases are separated and further upgraded to match with the ASTM and EN standards [16].

2.1.2.2. Pyrolysis and Gasification of wastes

Pyrolysis is an endothermic reaction that takes place at high temperatures in an inert atmosphere in which tree cuts or materials containing cellulose are converted into more valuable products having higher calorific value, such as char, bio-oil and flammable gases [17]. According to the reaction temperature, residence time and heating rate, the reaction produces different products [18]. At relatively low temperature, and low heating Rate 2-5 the product is mainly solid char, while relatively medium temperature, fast heating rate 450 and short residence time the product is mainly liquid bio-oil, if the desired product is flammable gases then the operating conditions are high operating temperature, fast heating rate 450 and long residence time [19]. On the other hand, gasification takes place at higher temperatures than that of pyrolysis and in presence of air. Partial oxidation occurs and the final product of this process is syngas, carbon monoxide and water vapour, then this gas mixture can be used for synthesis of higher hydrocarbons through the well-known Fischer-Tropsch process [20].

2.1.2.3. Biological processes for biofuels production

Biogas is the product obtained from anaerobic fermentation, digestion, of organic materials by micro-organisms under controlled conditions, temperature, moisture, pH, etc. [21]. Biogas is a mixture of gases mainly methane and carbon dioxide that results from anaerobic fermentation of organic matter by bacteria [22]. The possible wastes that can be used as a source for biogas production are agricultural wastes, animal manures, food wastes, industrial wastes and waste water [23]. Cellulosic wastes can be used for

production of bio-ethanol, which can replace fossil gasoline, through fermentation process [24]. After conversion the residues can be burnt for energy production. If the produced bio-ethanol will be used in vehicles engines then it should be further purified to remove solid particles, water content and associated sour gases such as carbon dioxide [25]. Wastes are pre-treated and conditioned before fermentation process to make the waste ready for conversion to the desired bio-ethanol product. Pre-treatment and conditioning steps include physical and chemical processes such as size reduction, screening and chemical or enzymatic hydrolysis [26].

3. WASTE TO ENERGY IN DIFFERENT COUNTRIES

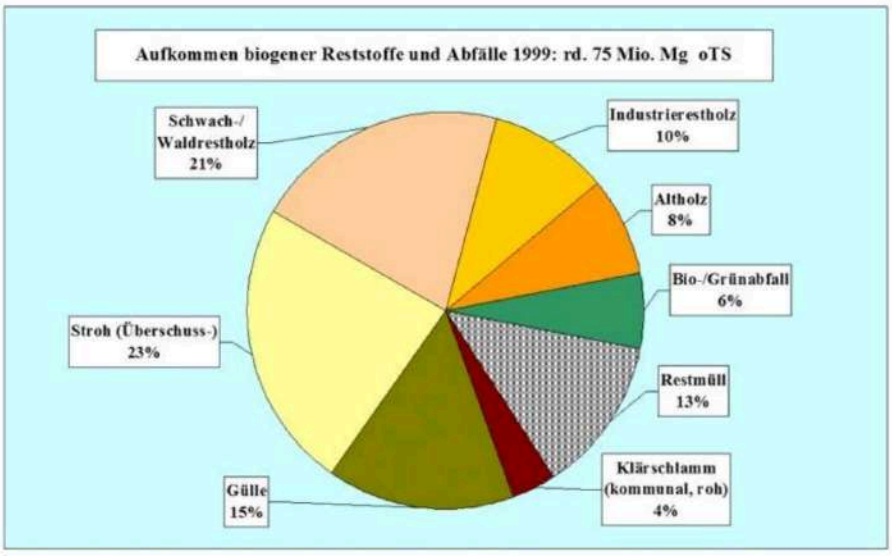
WTE concept is a dual benefit solution for waste problem since it will solve the fossil fuel shortage problem and decrease the environmental impacts associated with waste accumulation. According to Grand View Research the global WTE market is expected to increase by nearly half, from $25.3 billion in 2013 to $37.6 billion in 2020 [27]. So the WTE alternative must take a priority in solid waste management consideration for different countries.

3.1. India

India generates MSW at a rate of about 55 million tons per year and about 38 million cubic meters per year of sewage water [28]. The potential of using these wastes was discussed in many studies [29, 30]. The expected potential of power generation from sewage water or liquid municipal waste is about 226 MW while on using solid wastes the value increases to reach about 1457 MW, this means that the total potential of power production from wastes is about 1700 MW [31]. According to the ministry of New and Renewable Energy, there is a potential to recover 1,300 MW of power from industrial wastes, which is projected to increase to 2,000 megawatt by 2017 [32]. Projects of over 135 megawatt have been installed so far in distilleries, pulp and paper mills, and food processing and starch industries [33]. Two waste-to-energy plants producing 11 MW each were announced to be implemented in 2015 in Jabalpur and Hyderabad, besides a 12.6 MWplant at Nalgonda in Telangana, and 3 MW plant in Chennai and these plants will be commissioned by the end of 2016.

3.2. Germany:

The yearly MSW production in Germany is about 48 million tons [34]. As one of the high income countries, the average composition of German MSW is presented in table 7 [35].about 37.8% of the produced MSW are incinerated, 44.5% are recycled and 17.3% are composted while the remaining 0.4% goes to landfills. There are many WTE technologies applied in Germany such as mono-incineration, co-incineration, RDF production and biomethanation for biogas production. The average number of existing WTE plants in Germany are about 900 fermentation plants, 62 mechanical-biological waste treatment plants, 67 waste incineration plants, one pyrolysis plant and about 36 RDF power plants.



4. CONCLUSION:

From the above study it may be concluded that on planning for municipal solid waste management MSWM decision makers must take into account waste to energy alternatives according to economic, technical, legislative and environmental aspects. This research proposes a multi-objective WTE recovery systems performed through a variety of processes such as combustion, pyrolysis and gasification to achieve optimum performance. The results show that WTE can generate better solution, for MSWM, than that of the national practices compared to international trends.

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“Organic Aqua Regia”-Powerful Liquids for Dissolving Nobel Metals

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. SOUGATA SARKAR

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DATE: 11-01-2022

PLACE: RAHARA

“Organic Aqua Regia”-Powerful Liquids for Dissolving Nobel Metals

ABSTRACT:

The dissolution of noble metals is important for metallurgy ,catalysis, organometallic chemistry, syntheses and applications of noble-metal nanoparticles, and recycling of noble metals. Aqua regia (“royal water”) has been used for centuries as a powerful etchant to dissolve noble metals.

The beauty of aqua regia is that the simple1:3mixture of concentrated nitric and hydrochloric acids can dissolve noble metals such as gold, palladium, and platinum, although these metals are not soluble in either of the acids alone. The simple mixtures of thionyl chloride and some organic solvants/reagents can also dissolve nobel metals with high dissolution rates under mild conditions. This mixtures are called as “organicus liquor regius”. The discovery of this solvent system is off unprecedented scientific significance and engineering value : compared with inorganic chemistry, organic chemistry provides precise control over chemical reactivity, and the ability to tailor organic reactions enables the selective dissolution of nobel metals.

INTRODUCTION:

Recently, the author and his colleagues reported the discovery of a series of organic mixtures that dissolve various noble metals such as gold (Au), silver (Ag), and palladium (Pd) efficiently at room temperature (Lin et al., 2010). The author named these mixtures organicus liquor regius as the male counterpart of aqua regia (female) in Latin. For the readers to catch the term more easily, the author uses the term organic aqua regia (OAR) from here after. OAR is composed of thionyl chloride (SOCl2) and an effective organic component. By varying the composition and reaction conditions, selective dissolution of noble metals was achieved. The discovery of OAR and their potential applications in many fields have attracted extensive attention (Yeston, 2010; NatureEditorial, 2010; Urquhart, 2010; Ritter, 2010). The chapter provides a brief description of our work on, and understanding of, OAR from three aspects: discovery, fundamental chemistry, and some of the potential applications that have been preliminarily demonstrated.

SUMMARY OF THE PROJECT:

DISCOVERY OF OAR:

As many discoveries were, the discovery of OAR was accidental. In 2007, the author was involved in developing a chemical bonding process to anchor in situ functionalized vertically aligned carbon nanotubes to a modified Au surface. The basic chemistry was to assemble a thin layer of 4-mercaptobenzoic acid molecules on the Au surface, and then form the bonding between the functional groups (*e.g.*, hydroxyl groups) on the carbon nanotubes and the acid groups of the 4-mercaptobenzoic acid molecules via esterification. However, there were some

fundamental challenges to such a bonding process. First, solidsolid reaction at the interface was very unlikely to occur given the low functionalization degree of the carbon nanotubes and the irregular surface of the carbon nanotubes (at that time very few people talked about the irregular surface of the macroscopically well-aligned carbon nanotubes). Second, a wet chemical reaction at the interface was preferred, *e.g.*, a catalyzed esterification reaction in an aqueous solution. However, the wet chemical process—if not controlled well—would damage the vertical alignment of the carbon nanotubes (at that time very few people revealed the truth that a vertically aligned carbon nanotubes array/bundle could easily collapse in wettable liquids). Third, direct esterificaiton of benzoic acid with alcohol had been known to be very inefficient (Vulakh *et al.*, 1975; Zuffanti, 1948), and therefore, kinetically unlikely at the interface. To address these issues, the benzoic acid group was first transformed to the benzoic acid chloride group by the reaction with SOCl2 in the presence of a certain concentration of py as the catalyst. A dilute solution of SOCl2 (5~10 ppm) in acetonitrile (CH3CN) with a trace amount of py (py:SOCl2=1:2 in mole) was used.

DISSOLUTION OF DIFFERENT NOBEL METALS:

Noble metals, including Au, Ag and Pt, are scarce elements in earth's crust and greatly needed in high-tech applications.They are, therefore, precious and their demand is continuously growing. The possibility to recycle the elements from multi-metal materials such as printed circuit boards (PCBs) is crucial when sustainability and the circular economy are considered. In general, recovery of Au in the mining industry is most ly based on the hydrometallurgical cyanidation process, which relies on the use of stoichiometric amounts of cyanide salts and produces large amounts of hazardous waste.Consequently,a new and fairly unexploited concept known as dissolution of noble metals in organic solvents is highly attractive–it offers the possibility to develop benign and selective dissolution methods.One method is based on pyridine, dimethylformamide or imidazole solutions of thionyl chloride (SOCl2) called organic aqua regia (Fig. 1a) which, regardless of the toxicity of SOCl2, benefits from high selectivity towards Pt/Au/Pd and Au/Pd mixtures.Another method is based on somewhat toxic I2 using dithioxamides or tetraalkylthiuram disulfides (e.g. tetraethylthiuram disulfide Et4TDS) as donors to oxidize Au0 to AuIII. The third concept is based

on pyridinethiols but characterized by slow dissolution of Au in ethanol solutions (0.06×10-3 mol/(m2xh)).As thiols are commonly used as etch resists for Au0 surfaces, these results were intriguing and counterintuitive. Therefore, we took an initiative to carry out further studies and reveal mechanistic
details related to the 4-PSH-assisted dissolution.

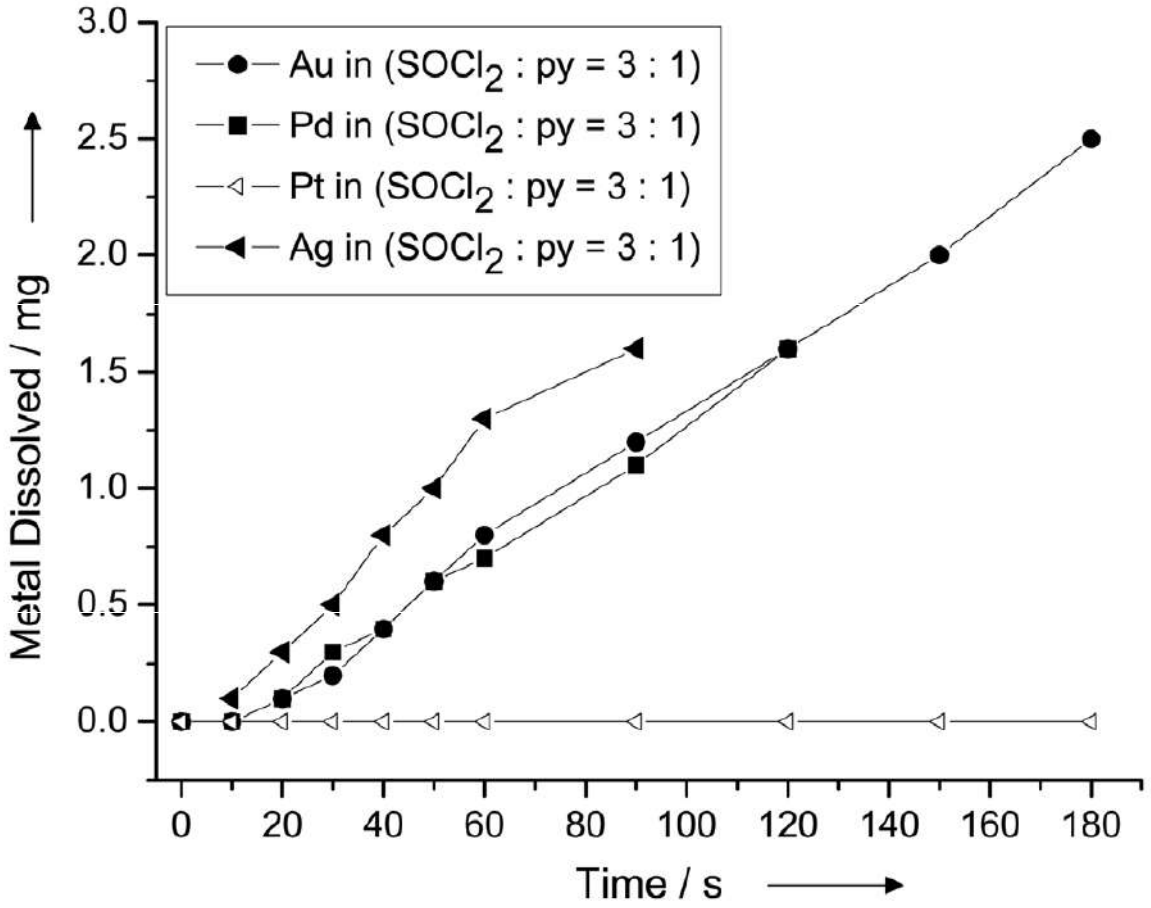

Fig. Kinetic studies of the dissolution of Au, Pd, Ag, and Pt in a 3:1 SOCl2-py mixture.

CONCLUTION:

Besides the application in the recovery of nobel metals, some potential applications of OAR such as itching of metal microelectronics industry, for instance for “vapor” itching of gold metallization on a circuit board by vaporized organic aqua regia and recovery of nobel metals from catalysis industry and consumer products are highly appreciated.

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A REVIEW

ON

SYNTHESIS AND CATALYTIC ACTIVITIES OF SILVER NANOPARTICLES

Project Work Submitted for Partial Fulfillment of the B.Sc. (Honours) Degree in Chemistry

BY

Prabir Mandal

Registration Number: A01-1152-112-043-2019 of 2019-2020

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Finally, my deepest admiration goes to my parents for their all-out support throughout my life.

…… ……

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Place: Sagar, South-24-Parganas.

SYNTHESIS AND CATALYTIC ACTIVITIES OF SILVER NANOPARTICLES

Introduction

In the last decade, green synthesis of metal nanoparticles has been exponentially increasing because of its various applications, such as electronics, catalysis, chemistry, energy, and medicine .In particular, silver nanoparticles (AgNPs) have many important applications in several fields, such as high sensitivity biomolecular detection and diagnostics , antimicrobials , catalysis ,Optics , biomedicine , medicine, as well as food and cosmetic industries .Conventional methods for manufacturing AgNPs, such as chemical reduction, electrochemical Process, photochemical reduction, laser ablation, hydrothermal method, microemulsion method, Radiation-induced, radiolytic reduction, sono-chemical reduction, pyrolysis, and lithography Are expensive, environmentally toxic, and/or hazardous.

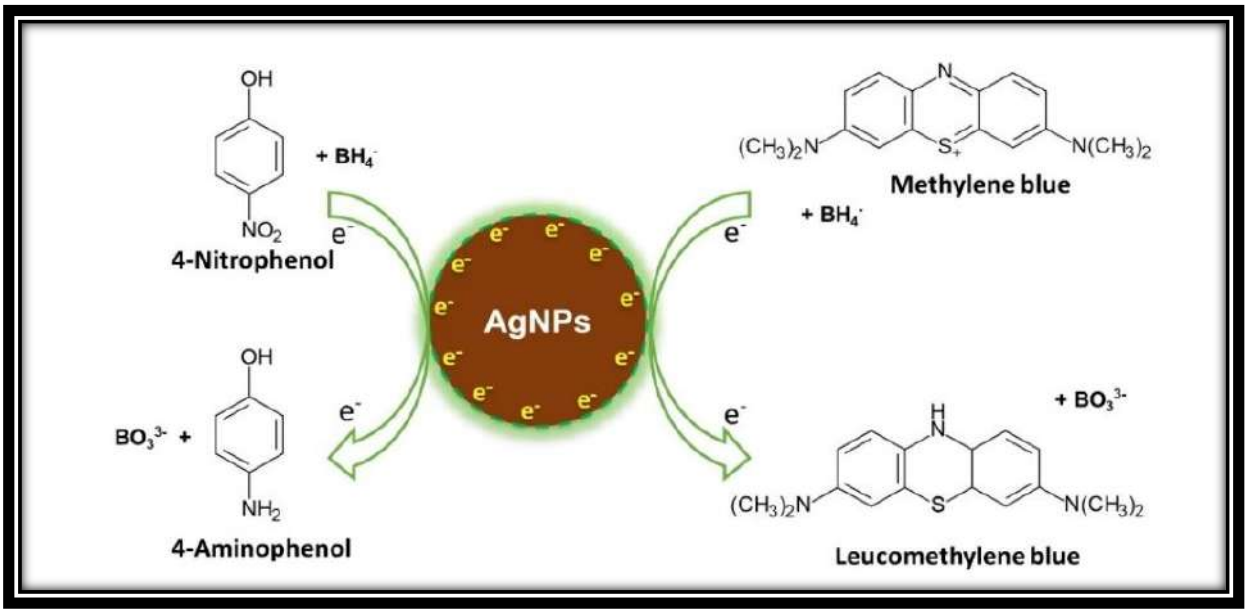
For example, the most typical chemical synthesis of AgNPs requires reducing agents such as sodium borohydride, hydroxylamine, sodium citrate, and hydrazine with environmentally undesirable solvents in some cases . In most cases, this produces biproducts that are harmful to the environment. Thus, green synthesis methods for AgNPs are highly required. The green methods should reduce the need for high pressure, high temperature, and toxic chemicals. They should also be simple (including only one step), rapid, cost-effective, and reproducible . Extracts from various plants, such as Solanum nigrum , Coleus aromaticus, Alpinia katsumadai , Acalypha indica , Clitoria ternatea[1].

Abstract

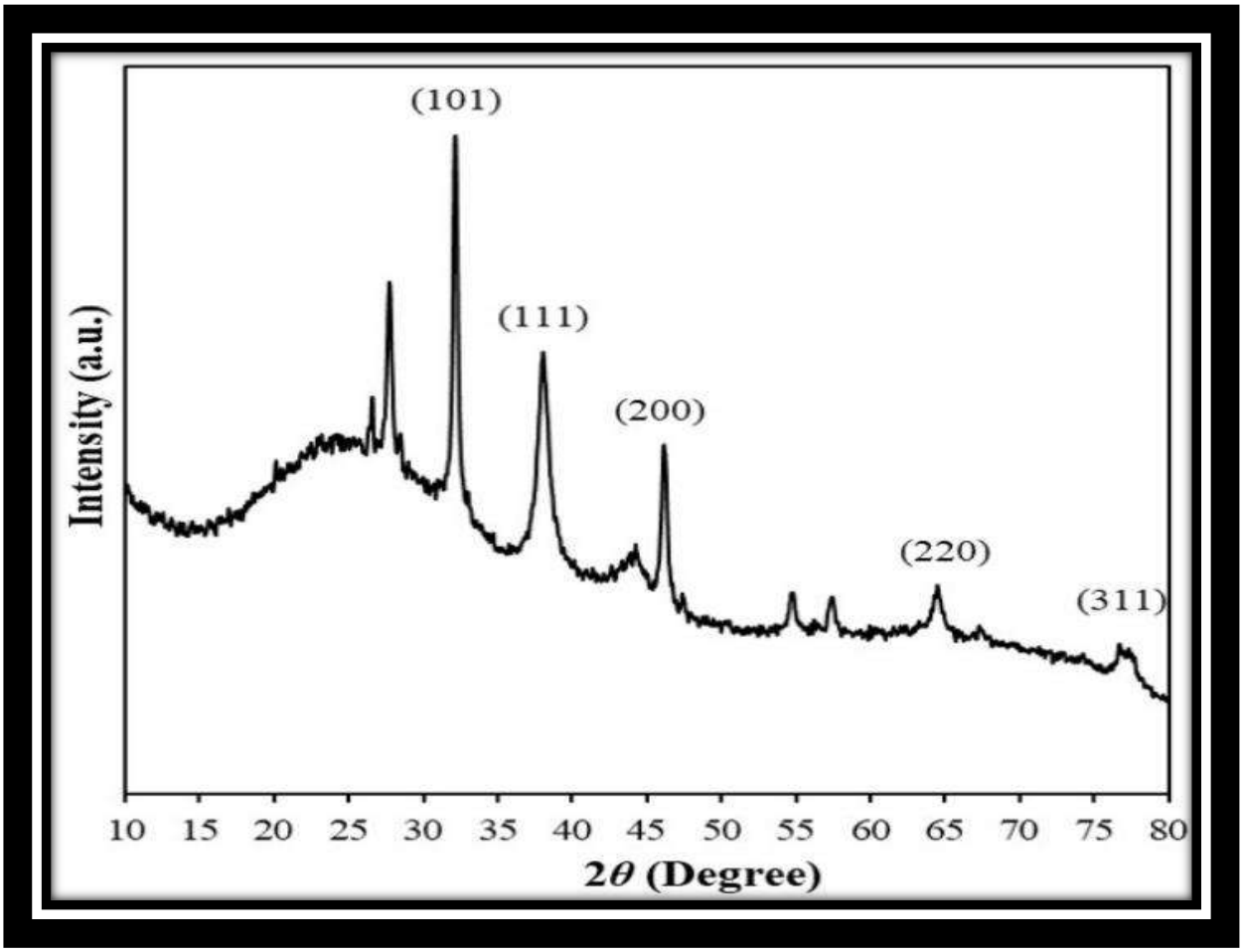
This work presents a simple method to produce silver nanoparticles through AgNO3 chemical reduction in a continuous media. Aminosilanes Act as catalytic reactors and superficial modifiers of Ag nanoparticles, inhibiting their growth and avoiding aggregation. Nanoparticles formation Is studied by UV–vis spectroscopy, atomic force microscopy (AFM) and dynamic light scattering (DLS) techniques. The extent of the reduction increases with either a higher aminosilane concentration or with aminosilanes with a higher number of amine groups. The number Of amine groups in the aminosilane has also a strong effect on the size of the resulting Ag particles. The morphology of the Ag nanoparticles Obtained is spherical and the mean size is of approximately 5 nm.

Synthesis of Ag Nanoparticles

An aqueous solution of AgNO3 (1 mM, 100 mL) was prepared in a volumetric flask, and the Flask was covered with carbon paper to prevent the autoxidation of silver. The aqueous stem

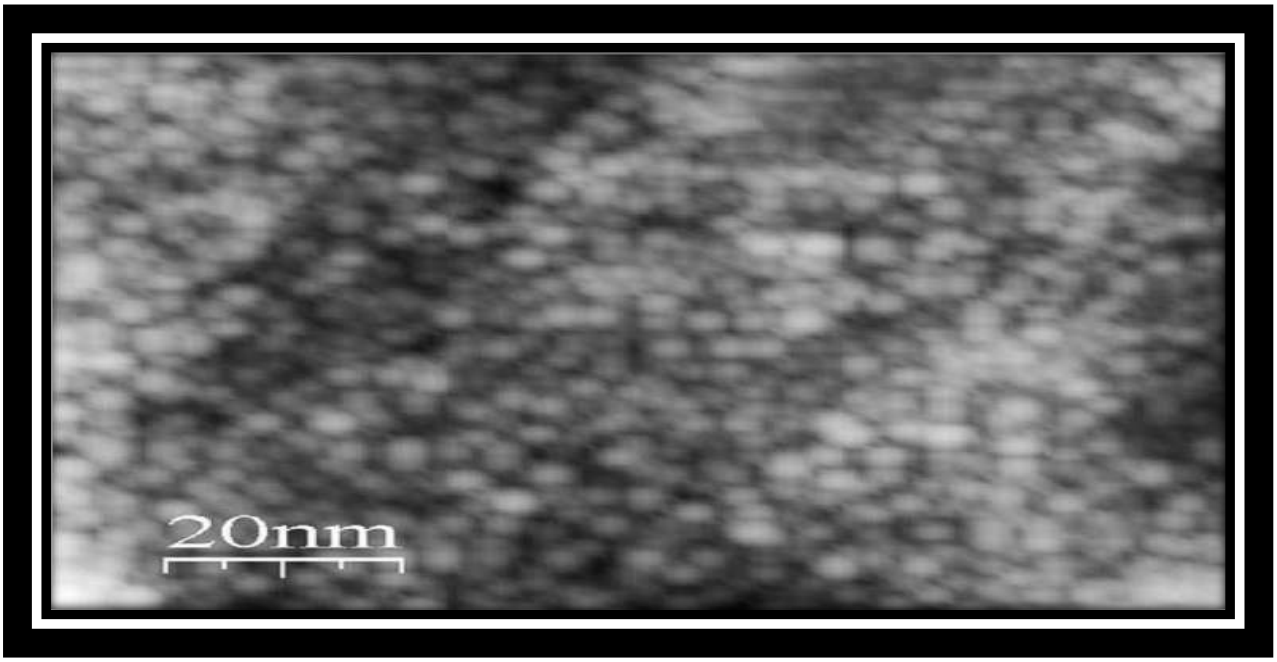


extract Piper chaba (4 mL) was placed in a conical flask. Then, the freshly prepared AgNO3 aq. (1 mM,80 mL) was added to the conical flask. The mixture was heated in an oil bath at 60 ◦C for 30 min under constant stirring. After this, the color of the solution changed from colourless to reddish brown. The resulting suspension was stored at room temperature for 48 h. The reaction mixture containing AgNPs was then centrifuged at 13,000 rpm for 30 min, and the precipitate was thoroughly washed three times with sterile distilled water to remove impurities.



X-ray diffraction (XRD) pattern of AgNPs synthesized using AgNO3 (1 mM, 40 mL) and Piper chaba extract (100 g/L, 2 mL) at 60 °C and pH = 7 for 1 h[1].

AgNPs were synthesized by in situ reduction followed by a coating with the stem extract of Piper chaba. The initial mixture was colourless and its color changed to reddish brown .After the reaction . The formation of AgNPs in the medium was confirmed by a Surface Plasmon Resonance (SPR) band and a UV-vis absorption peak corresponding to AgNPs at approximately 445 nm (Figure 3). Resulting AgNPs dispersed stably over 12 weeks, while AgNPs prepared by Conventional reduction with NaBH4 in the absence of stabilizing agent were precipitated within 12 hrs.



Two-dimensional (2D) AFM topographic image of Ag nanoparticles covered with ATS (1:5) placed over a mica substrate[2].

Catalytic Properties

Catalytic properties for propene cracking

Evaluation of catalytic performances toward soot oxidation is known To be highly dependent on the contact quality between soot and catalyst . Loose and tight contact modes as described earlier are commonly Studied, although intimate “supertight” contact was only described Recently by Aneggi et al. This latter study describes a high-energy Milling of CZ powder and carbon soot resulted in a thin carbon envelope Containing a core of oxide. We ought to study catalysts performance for Carbon oxidation under similar “supertight” contact. To obtain nano-Metric carbon layers covered the catalyst surface, propene cracking was Performed at 600 ◦C over both bare supports and silver supported catalysts for 30 min.

Soot oxidation activity was measured by TPO (Temperature Programmed Oxidation) of a mixture of a model soot (Printex U) and the Catalyst under 5% O2/He with an overall flow of 100 mL/min. Temperature ramp was 10 ◦C/min from room temperature up to 750 ◦C. Two Contact modes between model soot particles and catalyst grains were Investigated. The ‘tight” contact mode was obtained by grinding the Catalyst and the soot together in a ball-mortar containing two zirconia Balls of 5 mm diameter at 15 Hz for 2 min. “Loose” contact mixture was Obtained by only mixing the two

elements with a spatula for 5 min. “Tight” contact mode leads to improved contact between soot and Catalyst and is generally used to assess the intrinsic activity of the Catalyst toward soot oxidation.

The “Loose contact” mode is considered to be more representative of the poor contact quality obtained between a Catalyst wash-coat and soot particles trapped in a catalysed-DPF. TPO experiments reproducibility was checked by conducting experiments twice. Soot to catalyst mass ratio was ¼, 25 mg of the soot/-Catalyst mixture was introduced in a U-tube quartz reactor. Outlet gases (CO and CO2) were analysed by a micro-chromatograph from SRA. In Addition, the CO2 concentration was on-line measured with a Horiba IR Analyzer. Soot to gas conversion was obtained by integration of the Molar production rate of CO and CO2 with respect to time during soot Oxidation experiments, followed by normalization with respect to the Total amount of soot initially present in the reactor. Soot to gas conversion allowed for determination of T10 and T50 values, corresponding Respectively to temperatures at which 10% and 50% of the soot is converted to gas.

Conclusion

Ag nanoparticles dispersions, 5 nm average size, were obtained by chemical reduction of AgNO3 in aminosilanes alcoholic solution. Formation of Ag nanoparticles is favored with aminosilanes concentration increase and with the number of amine Groups in the aminosilanes. The number of amine groups in The aminosilane has also a strong effect on the size of the Resulting Ag particles. Colloidal solutions are stable for long periods and particles can be redispersed after the separation of their alcoholic Environment without modification of their properties. Aminosilanes act as superficial modifiers and catalytic reactors of Ag nanoparticles, inhibiting their growth and avoiding aggregation.

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ALCOHOLSAS AN ALTERNATIVE FUEL:

A BRIEF OVERVIEW

Project Work

By

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SUBMITTED for Partial Fulfilment of the B.Sc. Degree in Chemistry

Under the supervision of Dr. Subhabrata Banerjee

Registration No. : A01-1152-112-032-2019

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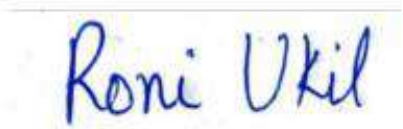

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ALCOHOLS AS AN ALTERNATIVE FUEL: A BRIEF OVERVIEW

Abstract

Since the middle of 1970s, the enthusiasm for using alcohols as alternate convenient fuels in internal combustion engine has been increased and it has reached peak stage by the middle of 1980s. The usage of alcohol as an alternate fuel, due to its minimal undesired effects on atmosphere, has gained importance. Harmful effects on environment are caused by various fossil fuels and their exhaust emissions such as carbon monoxide, carbon dioxide, hydrocarbons, nitrogen oxides and particulate matter Alcohol type of fuels is alternative to petroleum-based fuels due to reduced greenhouse gas emission, toxic exhaust emission and enhancement of overall energy efficiency. Moreover, they are convenient for internal combustion engines due to their high octane rating, burning velocities and wider flammability limits. In order to achieve better environmental sustainability, it is the right time to use lower molecular weight alcohols replacing other additives as octane boosters in automotive fuels in the present situation. In order to make the best use of alcohols as alternative fuels; one can redesign the engine or the vehicle can be redesign or one can blend in one or more additives to the ethanol or methanol to improve its characteristics. Catalytic conversion of synthesis gas to alcohols is advantageous, as this uses various renewable and non-renewable carbon resources. Different catalytic systems can be used for synthesizing higher alcohols from synthesis gas. Depending on the process conditions and the catalyst used, the reaction mechanism varies and the products include primary and secondary alcohols of both normal and branched carbon chains. The present paper includes an overview of the processes and catalysts used depending on the production of specific alcohols, as well as, the reaction mechanisms currently accepted. Transition metal-promoted alkali-modified molybdenum sulphide catalysts are considered to be more attractive to improve CO hydrogenation and for the production of linear alcohols.

• INTRODUCTION

Around the world, energy is one of the major sources for the improvement and development of human beings life standards and its sustainable development. With rapid growth in the world population during the past few decades, the energy requirements that have also increased at an even large rate in industrialization and transportation sectors lead to an increase in crude oil prices, which is directly affected by global economic activity [1]. Nowadays, worldwide 80% of fossil fuels consumed as primary energy, of which 58% of fossil fuels are consumed by the transportation sector only [2]. Since 1973, worldwide the primary energy demand has been increased at the rate of 2.0% on average per every year. As well as, still around one third of world's population are dependent on non-commercial fuels (United Nations 2007, 1). One of the significant environmental related issues is the widespread usage or burning of fossil fuels in many industries and transportation which are major contributors to air pollution, ozone depletion, global warming, climatic changes and human health-related problems. However, CO2 is an important pollutant, which is produced by improper combustion of fuel and other major pollutant is NO x, which is produced from both natural and man-made processes. Moreover, SO2 is one of the major air pollutants; it is released by the burning of fossil fuels like coal, petroleum and other factory combustibles. In the 1960s, environmental awareness was brought to public attention, when smog became a major issue in developed cities such as Mexico, Los Angeles and Tokyo City. According to National Energy Strategy in February, 1992, The United States of America used more than 185 million busses, cars and trucks for transportation, which consume two-thirds of the oil used by the United States. Likewise, in India 50% of oil was consumed for transportation in 1991; it has been increased to up to 61% by the year 2010. Day to day the oil usage was rapidly increased, it causes the severe damage of environment. In the year of 1992 June, Earth Summit conducted by the United Nations on Environment and Development (UNCED). In this summit

mainly the delegates all over the world aimed to decrease the global warming. Thus, the search for possible alternatives to fossil fuels becomes essential. In this regard, an ideal replacement would be characterized by renewable,sustainable, efficient, and cost effectiveenergy sources with fewer emissions [3,4]. Among many energy alternatives,alternative fuels are the most environment friendly energy source

A worrying statistical analysis is that, the global oil and gas production is approaching its maximum production level and the world is now finding one new barrel of oil for every four it consumes. Therefore, alcohol fuels are the best alternative to fossil fuels; alcohol fuels have been represented as a future leading supplier of energy sources that have the ability to increase the security of supply, reduce the amount of vehicle emissions, and offered a stable incomefor farmers. Right now, alcohol fuel used as alternative fuel instead of fossil fuelsin different motor vehicles (busses, cars, trucks, etc.) in most of the countries and Figure 1 shows the bus running withalcohol fuel [5].

Figure 1.
Alcohol fuel bus [5].

At present, the future of the world ecosystem is obviously the most important issue. Recently, our young researchers improved the awareness on environmental protection and usage of alcohol fuels or non-fossil fuels for internalcombustion engines. Generally, lowermolecular weight alcohols, particularlyethanol or methanol, comprise one group of alternative fuels which is considered attractive for

this purpose. The alcohol fuel has more advantages compared with fossil fuels, and they are given below:

- Both lower molecular weight alcohols can be made out of indigenous energy resources such as biomass, coal and natural gas, which are available with low cost.
- Combustion of alcohol in internal combustion engines (ICE) produces more combustion pressures compared to gasoline because of higher molal products to reactants ratio. Also, this improves power output and thermal efficiency compared to gasoline.
- Greenhouse gases emissions can be reduced.
- Alcohol fuels have a lower evaporative emission.
- The leaks and spillages of alcohol fuel from the oil tankers; alcohols are miscible in water and could be washed out with water for quick and easy removal. They are easily metabolized if absorbed by the ground.
- The negligible amount of ash was released into the atmosphere by the combustion of alcohol fuel in ICE due to presence of less carbon content in alcohol fuel.
- The overall energy efficiency of fuel can be improved.

Table 1 gives a brief account of gasoline properties, their desirable impact on engine performance, and their undesirable impact on the environment .

Table 2 compares the properties of alcohols such as boiling point, latent heat, vapour pressure and solubility in water, with those of octane and hexadecane [6].Compared to conventional fuels, alcohols have less combustion energy. However, the lowest stoichiometric air to fuel ratio helps alcohol fuels to produce more power inside an engine when these fuels are burned. Table 3 shows the effective blending values of oxygenated fuels as gasoline blends [7]. Research Octane Number (RON) is determined in test engines at a relatively low speed (600 rpm) to simulate city driving speed with frequent acceleration. Motor octane number (MON) is measured at a higher speed (900 rpm), which simulates highway driving. For most fuel components, RON is greater than MON and the difference between them is used to judge fuel quality. This is

known as the sensitivity of the fuel and a maximum value is specified for the gasoline, which typically should be less than 10. Although methanol has the highest percentage of oxygen, its sensitivity is 30 when compared with ethanol, having a sensitivity of 15 and a Reid vapour pressure (RVP) much less than that of methanol. In essence, ethanol is more advantageous when comparing the percent oxygen content, sensitivity, and Reid vapour pressure with those of other fuels.

· Catalyst Support For Higher Alcohol Syntheses

· High pressure, high temperature methanol synthesis catalysts:

Natta et al. first studied the synthesis of alcohols from synthesis gas over ZnO/Cr2O3 catalysts promoted with alkali metals, these are high pressure and high temperature methanol synthesis catalysts. They reported that Cs, Rb, and K were the most active promoters for production of HAS. The HAS takes place over this catalyst at high temperatures of 400-450 ◦C and at high pressures of 10-25.5 MPa. These catalyst systems represent an improvement in the selectivity towards iso-butanol, but the total product rate of alcohols in the product stream is lower than that of Cu-containing catalysts . These catalyst systems require high operating temperatures and pressures, are relatively inactive, and yield branched alcohols, among which iso-butanol is the main product and methanol is the other product . The activities and selectivities of alcohols obtained over high pressure, high temperature methanol synthesis catalysts are compared in Table 4. The commercially available Zn/Cr spinel support promoted with K is compared with the catalyst supported on ZnO powder. The total alcohols and iso-butanol space time yield (STY) increases whereas, the methanol and hydrocarbon STY decreases with the addition of K. The best operating parameters for the production of higher alcohols are 440 ◦C and 10.3 MPa (1500 psi) using H2 to CO molar ratio of 1.0 and gas hourly space velocity (GHSV) of 12,000 over the 1 wt% K promoted catalyst supported on commercial Zn/Cr spinel. When compared with K, incorporation of Cs in Zn/Cr catalysts increased the higher alcohol production rate and selectivity.

Table 1
Summary of gasoline properties [4].

Gasoline property	Desirability	Impact on environment
Octane number	Avoid engine knocking; increase fuel–air mix compression ratio, engine power, and efficiency	Octane boosting compounds are not environmentally friendly: – Lead additives are toxic air pollutants and poison catalytic converter catalysts. – Benzene is carcinogenic. – Aromatics produce more smoke and smog – Olefins form engine fouling gums, more smoke and smog
Volatility (Reid vapor pressure)	Sufficient light components to give adequate vaporization of fuel air mix for easy engine cold start	– Too many light components result in hydrocarbon loss & result in atmospheric pollution. – Too many heavy components contribute to chamber deposits & spark plug fouling causing release of unburnt hydrocarbons into the atmosphere.
Sulfur content	Not desirable	– Sulfur compounds are corrosive, foul smelling, and increase sulfur trioxide emissions. – Decreased catalytic converter efficiency. – Adversely affect ignition timing, leading to lower engine efficiency.
Olefins	Desirable for their octane value	– Leads to deposits and gum formation; increased emissions of ozone forming hydrocarbons, and toxic compounds.
Aromatics	Desirable for their octane value	– Increased engine deposits and tailpipe emissions, including carbon dioxide. – Produces carcinogenic benzene in exhaust.
Stability additives	Reduce valve deposits	– Affect carburetors resulting in higher H/C and CO emissions.

Table 2
Characteristics of chemically pure fuels [5].

Fuel	Chemical weight (lb/mol)	Specific gravity	Boiling point (°C)	Latent heat (Btu/lb)	Combustion energy (Btu/lb)	Vapour pressure @100 F (psig)	Solubility part in 100 parts H_2O	Stoichiometric air-fuel ratio
Methanol	32	0.79	65	503	10,260	4.6	Infinite	6.5
Ethanol	46.1	0.79	78	396	13,160	2.2	Infinite	9
Butanol	74.1	0.81	117	186	15,770	0.3	9	11.2
Octane	114	0.70	210	155	20,750	1.72	Insoluble	15.2
Hexadecane	240	0.79	287	-	20,320	3.46	Insoluble	15

Table 3
Effective blending values of the fuels [6].

Fuel	Density (kg/l)	% of O_2 (wt%)	RON	MON	RVP (kPa)
Methanol	0.796	49.9	130	100	250
Ethanol	0.794	34.7	115	100	130
IPA	0.789	26.6	117	100	70
TBA	0.791	21.6	100	90	65
MTBE	0.744	18.2	110	100	55
ETBE	0.770	15.7	112	100	28

Table 4
Comparison of the activities of high pressure, high temperature methanol synthesis catalysts [30].

	Catalyst					
	Zn/Cr commercial support	1 wt% K/Zn/Cr commercial support	1 wt% K/Zn/Cr commercial support	1 wt% K/Zn/Cr commercial support	1 wt% Cs/Zn/Cr commercial support	1 wt % K/ZnO support
Temperature (°C)	440	400	400	440	440	440
Pressure (MPa)	10.3	6.9	10.3	10.3	10.3	10.3
H_2/CO molar ratio	1.0	1.0	1.0	1.0	1.0	1.0
GHSV (h^{-1})	12,000	12,000	12,000	12,000	12,000	12,000
CO_2-free CO conversion (%)	14	12	19	19	16	8
STY of total alcohols (g/g_{cat} h)	0.133	0.133	0.251	0.167	0.154	0.157
STY of methanol (g/g_{cat} h)	0.102	0.078	0.170	0.049	0.032	0.142
STY of ethanol (g/g_{cat} h)	0	0	0	0	0	0
STY of n-propanol (g/g_{cat} h)	0.018	0.008	0	0.009	0.005	0.006
STY of iso-butanol (g/g_{cat} h)	0.013	0.047	0.081	0.103	0.115	0.008
STY of hydrocarbons (g/g_{cat} h)	0.094	0.048	0.046	0.101	0.081	0.023
CO_2-free selectivity of total alcohols (%)	43	27	75	53	57	70

· Some Reactions For Higher Alcohol Synthesis

Smith and Anderson assumed the following growth rules to describe a chain growth scheme for the synthesis of alcohols from syngas over modified methanol synthesis catalysts[31]: Higher alcohol formation results from the reaction of two intermediates of lower carbon numbers. At least one of these has a carbon number of one or two. Thus, growth is by one or two carbon additions only. Addition occurs at the - or -carbon (with respect to the hydroxylated carbon atom) of the reaction intermediate. Addition does not occur on -CH group. Two-carbon addition does not occur at an -carbon. All the reaction rates are assumed to be first order with respect to the concentration of growing intermediate at the surface, including desorption of this intermediate. The rate constants are also assumed to be independent of carbon number and all steps are irreversible. Based on these assumptions, the following reaction scheme represents the successful kinetic model for the formation of methanol and higher alcohol from CO and CO_2 on modified methanol synthesis catalytic sites.

Reaction schemes for methanol synthesis from CO and H_2 are

$$CO + s \rightarrow COs$$

$$H_2 + 2s \rightarrow 2Hs$$

$$COs + Hs \rightarrow HCOs + s$$

$$HCOs + Hs \rightarrow H_2COs + s$$

$$H_2COs + Hs \rightarrow H_3COs + Hs$$

$$H3COs + Hs \rightarrow CH_3OHs + s$$

$$CH_3OHs \rightarrow CH_3OH + s$$

Reaction schemes for methanol synthesis from CO_2 and H_2 are

$CO2 + s \rightarrow CO2,s$

$H2 + 2s \rightarrow 2Hs$

$CO + s \rightarrow COs$

$CO2,s + Hs \rightarrow HCO2,s + s$

$HCO2,s + Hs \rightarrow H2COs + Os$

$H2COs + Hs \rightarrow H3COs + Hs$

$H3COs + Hs \rightarrow CH3OHs + s$

$CH3OHs \rightarrow CH3OH + s$

$COs + Os \rightarrow CO2,s + s$

Reaction schemes for higher alcohol synthesis from CH_3OH only are

$CH_3OH + s \rightarrow CH_3OHs$

$CH_3OHs + s \rightarrow CH_3Os + Hs$

$CH_3Os + s \rightarrow CH_2Os + Hs$

$CH_3Os + CH_2Os \rightarrow CH_3CH_2Os + Os$

$CH_3CH_2Os + Hs \rightarrow CH_3CH_2OHs + s$

$CH_3CH_2OHs \rightarrow CH_3CH_2OH + s$

$COs + Os \rightarrow CO_2,s + s$

$CO_2,s \rightarrow CO_2 + s$

$CO + s \rightarrow Cos$

$H_2 + s \rightarrow H_2,s$

The higher alcohols formed include ethanol, 1-propanol, 2- butanol, 2-methyl-1proponol, 1-butanol, and pentanols.

• Conclusions

The production of alcohol fuel has gradually increased and become an important industry in various countries such as the United States, Brazil, and China. Methanol was produced from biomass or coal and natural gas while ethanol is mainly produced from food crops or sugarcane molasses by fermentation process. So that, rural area's sugarcane industry is one of the major industrial corridors, meanwhile the agriculture economy was increased and generates employment for more people by the collaborating with sugar industry either directly or indirectly. After production of methanol or ethanol, it was blended with petrol/gasoline in different proportion like E10 considered as low-level ethanol blends and E85 considered as high-level ethanol blends. Day to day, the usage of alcohol fuels has been rapidly increased due to their positive impacts such as reducing GHG emissions, reduction in the emission of toxic gases, and helping to mitigate climate change. Likewise, it has an impact on sustainable development in economic, social and environmental aspects. Therefore, alcohol fuel can be used as best transportation fuel instead of gasoline, but it is still years far away from extensive adoption. More researches and improvements are necessary if we are to use alcohol as a fuel of the future. Catalytic conversion of synthesis gas to alcohols is advantageous as this uses various renewable and non-renewable carbon resources. Different catalytic systems can be used for synthesizing higher alcohols from synthesis. gas. Depending on the process conditions and catalyst used, the reaction mechanism varies and the products include primary and secondary alcohols of both normal and branched carbon chains. Transition metal-promoted alkali-modified molybdenum sulphide catalysts are considered to be more attractive to improve CO hydrogenation and for the production of linear alcohols.

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INTERFACIAL SYNTHESIS OF HOLLOW METAL-ORGANIC FRAMEWORK CAPSULES AND THEIR DIFFERENCE IN PROPERTIES

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. SOUGATA SARKAR

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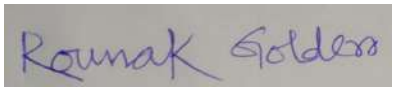

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INTERFACIAL SYNTHESIS OF HOLLOW METAL-ORGANIC FRAMEWORK CAPSULES AND THEIR DIFFERENCE IN PROPERTIES

ABSTRACT :

Metal-organic frameworks (MOFs) are a class of crystalline materials that consist of metal ions and organic ligands linked together by coordination bonds. Because of their porosity and the possibility of combining large surface areas with pore characteristics that can be tailored, these solids show great promise for a wide range of applications. Although most applications currently under investigation are based on powdered solids, developing synthetic methods to prepare defect-free MOF layers will also enable applications based on selective permeation. Here, we demonstrate how the intrinsically hybrid nature of MOFs enables the self-completing growth of thin MOF layers. Moreover, these layers can be shaped as hollow capsules that demonstrate selective permeability directly related to the micropore size of the MOF crystallites forming the capsule wall. Such capsules effectively entrap guest species, and, in the future, could be applied in the development of selective microreactors containing molecular catalysts.

INTRODUCTION:

Metal-organic frameworks(MOFs) are a new class of materials that have been intensely studied in recent years. A typical MOF is comprised of metal ions connected by organic bridges forming a well-defined repeating framework. Due to regularity of their microstructures and variety of possible construction units, MOFs possess potential applications in such areas like separation, filtration, catalysis and gas storage etc.

There are currently two general approaches to the preparation of MOF-based membranes. The first approach is to grow MOF membranes in situ or by secondary growth after seeding from a supporting membrane. In contrast to in-situ or seeding/secondary growth of MOFs in the first approach, the second approach is to incorporate pre-synthesized MOFs into matrix materials to form mixed matrix materials(MMMs).

The interface between two immiscible liquids offers a scaffold for the controlled formation of thin layers with various compositions. A spherical liquid-liquid interface obtained for instance, by dispersing one solvent phase, as droplets, in the other, similarly facilitates the preparation of hollow shells. Metal-organic frameworks (MOFs) are composed of metal centres bridged by organic ligands, resulting a network with uniform pores of molecular dimensions. Because of this combination of inorganic and organic building units in their crystal lattices, MOFs are often referred to as hybrid framework compounds.

A MOF crystal lattice is formed through the reaction of metal ions and linking ligands, which are introduced into a synthesis mixture of inorganic and organic precursors respectively. Because these precursors have markedly different solubility characteristics. This MOFs are very different from the properties of the main complex.

Here we demonstrate how the difference in solubility characteristics of the organic and inorganic MOF precursors can be used in a synthetic approach. Comprising two immiscible solvents, crystallization takes place only at the liquid-liquid interface. This interface can be used as a template for the formation of a MOF layer.

SUMMARY OF THE PROJECT:

In all methods for synthesizing MOF films reported to date, the metal ions and ligand molecules applied to a film growing at a support-liquid interface have been supplied from the same direction. This has led to problems such as undesired nucleation in the solution or growth on top of previously formed crystals instead of in the support, resulting in incomplete support coverage and uneven membrane thickness. Such problems have had to be circumvented by enhancing the surface affinity of the support for one of the MOF precursors or by implementing a separate seeding step. The ligands and metal ions approach the growing MOF film from opposite directions, allowing the growth to self-conplete in just a single step. During the growth process, diffusion of the MOF precursors will be faster ar the remaining defects than through the already formed layer, and new crystallites will be formed primarily at the defect sites, thereby sealing the gaps.

The growth mechanism described above has been used to generate hollow capsules of the widely investigated, MOF material [Cu3(BTC)2], which consists of Cu(II) ions linked together by 1,3,5-benzenetricarboxylate(BTC) ligands. The classic synthesis of [Cu3(BTC)2] involves mixing an aqueous solution of a cupric salt with a solution of 1,3,5-benzenetricarboxylic acid(H3BTC) in

ethanol followed by hydrothermal treatment. By replacing ethanol with a longer chain alcohol such as 1-octanol, a biphasic synthesis mixture is obtained.

It can easily be envisioned that layering one solution on top of another immiscible phase leads to a flat interface, and therefore a flat MOF membrane when each phase contains one of the precursors, namely copper acetate and H3BTC. On bringing the two solutions into contact, nucleation and growth of [Cu3(BTC)2] occurs via a ligand exchange mechanism at the copper centre. In aqueous solutions of copper acetate, the dominant structural unit is the acetate-bridged paddle-wheel structured Cu(II) diner [Cu2(CH3COO)4(H2O)2]. At the interface between the aqueous and organic solutions, exchange takes place between the carboxylate groups of the bridging acetate ligands and those of the BTC ligands to form isostructural secondary building units, copper paddle-wheel structured Cu(II) dimers [Cu2(BTC)4(H2O)2]. The [Cu3(BTC)2] crystal lattice is formed by linking these building units together through the remaining carboxylate groups on the BTC ligands.

Similarly, dispersing the aqueous solution as droplets in a 1-octanol phase leads to the formation of hollow capsules, because the droplets, rather than a flat interface. The aqueous cupric acetate solution was introduced into the co-flowing organic ligand solution through a tapered capillary. Droplets detached from the capillary when the forces exerted by the co-flowing continuous phase exceeded the force due to interfacial tension. Subsequently, droplets travelled through the hydrophobic tubing, and the ligand molecules were able to react at the interface and from the capsule wall.

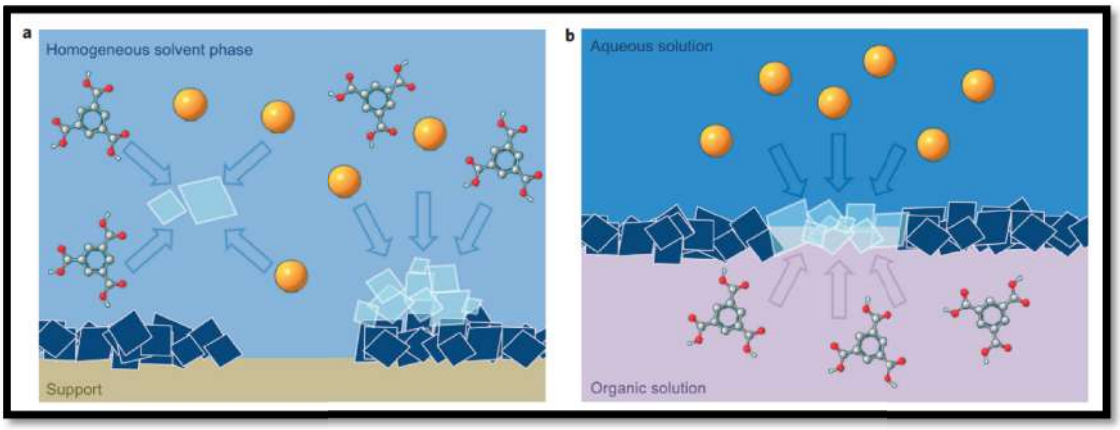

FIG: Different concepts in the synthesis of MOF films.

a: Deposition of a MOF layer on a support (brown) in a homogeneous synthesis mixture. Undesired nucleation in solution or growth on top of previously formed crystals can occur.
b: Interfacial preparation of a MOF layer using a biphasic synthesis mixture consisting of an aqueous metal-ion-containing solution (blue) and an organic ligand solution (purple).

Given the continuous-flow nature of capsule synthesis, control over crystallization kinetics is essential to keep tubing to a practical length. To avoid a reduction in crystallization rate due to reactant depletion near the interface, the concentrations of both the ligand and metal salt solutions were close to maximum solubility in either phase(70 mM and 360 mM respectively). In addition, the selection of Cu(II) acetate as the metal ion source proved beneficial in decreasing the capsule preparation time when compared to Cu(II) nitrate. Elemental analysis confirmed the absence of nitrogen compounds in the resulting [Cu3(BTC)2] material.

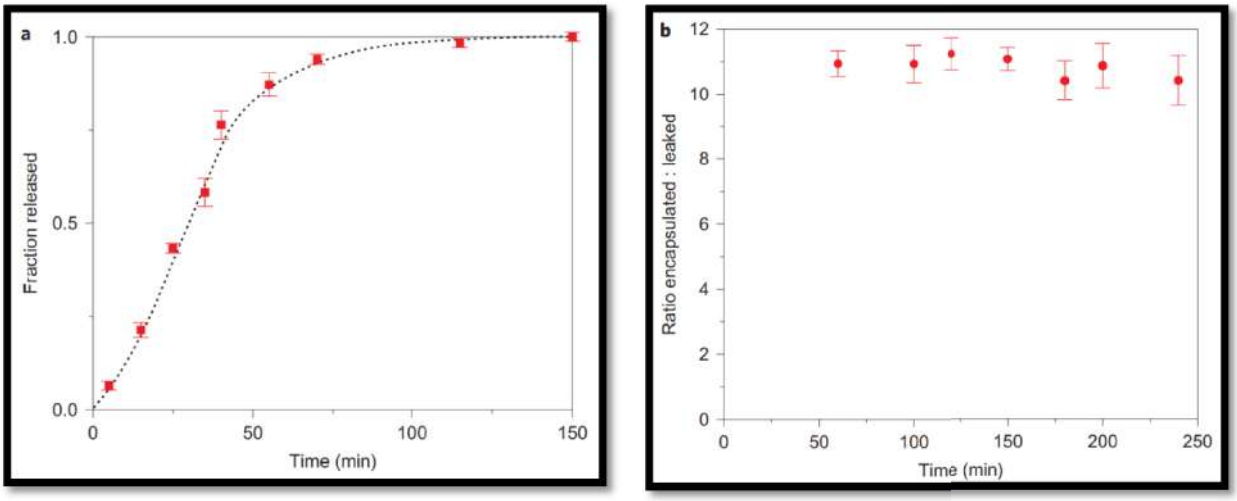

FIG : Selective permeability of [Cu3(BTC)2] capsules.

a : Release of the small molecule ethylene glycol through the capsule wall. Experimental data (red squares) are well described by a Fickian diffusion model (black squares) for a diffusivity of 5 × 10211 cm^2 s 21 in the microporous capsule wall.

b : Encapsulation of the large dye molecule Rose Bengal. The experimental ratio of dye molecules inside and outside the capsules (red circles) remains constant over time, confirming effective encapsulation. In both graphs, error bars indicate standard deviation

The crystallization process and the properties of the resulting capsule walls can be adjusted further by using additives in the aqueous phase. To avoid coalescence of the droplets, a small amount of the water-soluble emulsifier polyvinyl alcohol (PVA) can be added to the interior phase. Because biphasic synthesis is based on precursors that encounter one another exclusively at the interface of two immiscible solvents, the delineation of this interface layer is of great importance in determining the structure and thickness of the resulting material. Exchanging 1-octanol with another water-immiscible alcohol,such as cyclohexanol, has a negligible influence. However, by adding ethanol to the templating aqueous droplets, the liquid–liquid interface becomes less well-defined as the ethanol diffuses out. As a consequence, reaction between MOF precursors

is less strictly confined to a thin layer capsules form an enclosed space and that all micropores in the MOF crystal lattice have exactly the same dimensions, the integrity and permeability of the MOF membrane that forms the capsule wall can be probed by including molecules of different size in the inner phase during synthesis. Molecules smaller than the micropores in the [Cu3(BTC)2] crystal lattice should be able to diffuse freely through the MOF membrane. Ethylene glycol was therefore included in the water phase as a small probe molecule. Monitoring the release of ethylene glycol from the capsules to the surrounding solvent over time yields a release profile.

In the case of a defect-free membrane, molecules larger than the micropores of the [Cu3(BTC)2] crystal lattice should be retained within the capsule. To test this, the water phase that templates the interior of the droplets was spiked with Rose Bengal, a large dye molecule that neither disturbs the crystallization nor is incorporated in the micropores during crystallization. After collection of the capsules, the dye content in the surrounding solvent was determined by UV–vis spectroscopy following an incubation period at room temperature. The capsules were then broken by sonication to release the encapsulated dye molecules and the dye content was sampled again after centrifugation. Repeating this experiment for different incubation periods up to 4 h proves the effective encapsulation of the dye, because the ratio of dye molecules inside and outside the capsules remains unaffected throughout the duration of the experiment.

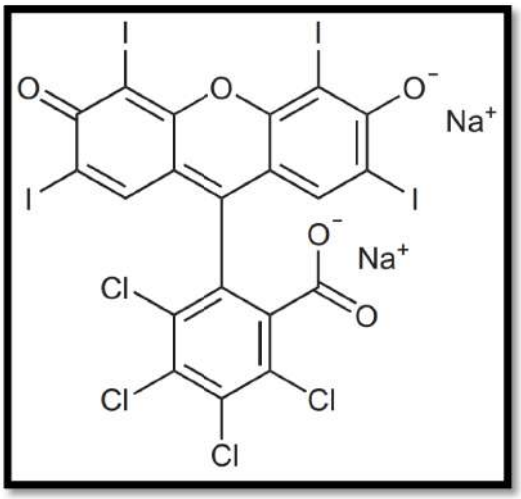

FIG : Rose Bengal

Given the intrinsically hybrid nature of all MOFs, the interfacial growth method can also be extended to other MOF structures,including the intensely studied material ZIF-8, which is a prime candidate for gas separation membranes. Also, as [Cu3(BTC)2] capsules are formed under mild conditions, further experiments are aimed at encapsulating functional organic species during synthesis other than the dye molecule Rose Bengal. Indeed, if only substrate molecules with appropriate dimensions can reach the catalyst through the uniform micropores in the shell, reactant size selectivity would not need to be a characteristic of the catalyst itself, which consequently could be chosen on the basis of reactivity alone, for example. Moreover, because the catalyst is merely enclosed in a sealed compartment, it essentially remains homogeneous. Therefore, a decrease in

activity or selectivity, as is sometimes observed on anchoring a homogeneous catalyst to a solid support, is unlikely.

CONCLUSION:

The results presented here illustrate a synthetic approach ideally suited to preparing layers of MOFs by taking advantage of the hybrid nature inherent to this class of materials. The difference in solubility characteristics of the organic and inorganic precursors enables the self-completing interfacial formation of a MOF layer in a biphasic synthesis mixture, as the two precursors encounter each other from opposite sides of the liquid–liquid interface. Moreover, in the absence of a support, freestanding MOF layers are obtained that can be shaped as hollow capsules by droplet templating. The size-selective permeability displayed by such capsules, together with the mild synthesis and activation conditions that allow encapsulation of functional species during synthesis, makes these hollow structures interesting candidates for application as microreactors.

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Sonogashira Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts

Project Work

Submitted for Partial Fulfilment of the B.Sc. Degree in Chemistry

by

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Registration No. A01-1112-112-026-2019

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CERTIFICATE

Date: 27.01.2022

This is to certify that the project work entitled "Sonogashira Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts" submitted by **Mr. Sagnik Pal** (Registration No. A01-1112-112-026-2019) for the partial fulfilment of the B. Sc degree in Chemistry at Ramakrishna Mission Vivekananda Centenary College, Rahara has been executed under my supervision.

Buddhadeb Dutta

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Sonogashira Coupling Reactions Catalyzed by Heterogeneous Palladium Catalysts

ABSTRACT:

Using heterogeneous catalysts, with the proper choice of solvent medium in Sonogashira coupling of a wide variety of aryl bromides, aryl iodides, bromo pyridines, bromo pyrans got adequate amount of yield. Furthermore, the catalyst could be recycled without any loss of activity.

INTRODUCTION:

Among various coupling reactions palladium catalysis have much relevance and importance. We use Pd catalysis in coupling reactions like Sonogashira, Stille, Suzuki, Heck reactions. Using this methodology synthesize of many products becomes much more efficient with higher reaction rate, higher turnover numbers (TON) besides those sometimes we get more yield and high selectivities. This type of catalysis with proper ligand designing can provide improved lifetime of weak leaving group (e.g., chloride) and increased stability to occur the reactions without at lower temperature and the exclusion of water or air. Besides many relevance, importance of homogeneous Pd catalysts have many drawbacks such as expensiveness of Pd metal, reuse and recycling of the catalysts is pretty much difficult. So, these are still challenges to overcome.[1-7]

Considering these problems, heterogeneous Pd catalysis is more convenient to use. Here, Pd is fixed to a solid support,[5,8] such as activated carbon (charcoal),[9-11] organic polymers,[8] zeolites and molecular sieves,[8,12-16] metal oxides[8,17-19] (mainly silica or alumina), alkali and alkaline earth salts ($CaCO_3$, $BaSO_4$, $BaCO_3$), clays,[20,21] porous glass,[22] or polymers embedded in porous glass.[23] Heterogeneous catalyst can be separated after reactions or reuse it until it's not deactivated. Though in case of heterogeneous catalysts, supported Pd catalysts are require more drastic condition than homogeneous catalysts, it's not a problem because heterogeneous catalysts are often relatively more stable. The application of supported Pd was introduced relatively late (early 1970s) into Pd catalyzed coupling reactions but it has been increasingly used up to now. Some industrial applications have already been developed.[25,26]

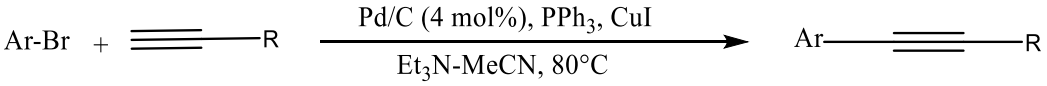
The coupling of terminal alkynes with aryl or vinyl halides under palladium catalysis is known as the **Sonogashira Coupling Reaction**. This process is one of the important and widely used carbon-carbon bond-forming reactions in organic synthesis. Use of a heterogeneous palladium catalyst such as a solid-supported metal. The most readily available form of supported catalyst is palladium on charcoal, which is widely used in heterogeneous hydrogenation processes and also has a growing importance in carbon-carbon bond-forming reactions.[44,45] We can also use as heterogeneous catalyst in Sonogashira Coupling are Pd on metal oxides, Pd on modified silica, Pd on microporous and mesoporous support, Pd on clay and other inorganic materials. With heterogeneous catalysts Sonogashira coupling reaction requires the presence of a base, and generally CuI is used as co-catalyst but it is possible to perform this reaction without copper. The advantages of Sonogashira coupling reaction are the mild conditions usually employed, reaction is often done in room temperature, the ease of separation and facile recycling of the Pd metal and the low level (usually below 1 ppm) of metal contamination[45d] in the product.

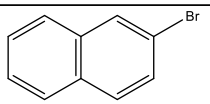
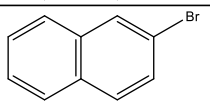
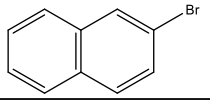
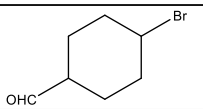
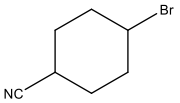
Songashira Coupling Reactions

(1a) Pd on Carbon (Pd/C); In Anhydrous Media

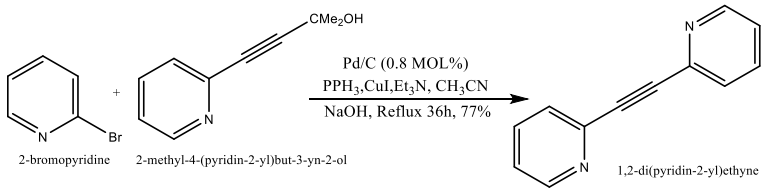
In Pd/C -ctalyzed Sonogashira coupling reactions Guzman and his co-workers invented that in the presence of PPh_3 and CuI in an anhydrous mixture of triethylamine and acetonitrile, aryl bromides coupled with trimethylsilylacetylene, phenyl acetylene and butene.[29]. Here notably, got higher yields of the products than previously reported homogeneous Pd(0) catalysts reactions. So, for Sonogashira coupling reactions Pd/C-PPh_3-CuI becomes an efficient catalytic system.

Pd/C-Catalyzed Sonogashira Coupling of Aryl Bromides with Acetylenes[29]

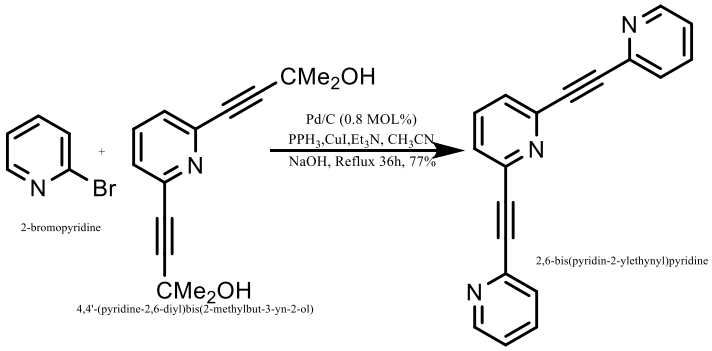


	Ar-Br	R	Yield (%)
1		Ph	58
2		$SiMe_3$	88
3		Et	73
4		Ph	64
5		Ph	59

Pd/C-PPh_3-CuI catalytic system can be used to synthesize 1,2-di(pyridin-2-yl)ethyne by coupling of 2-bromopyridine[30] with 2-methyl-4-(pyridin-2-yl)but-3-yn-2-ol .



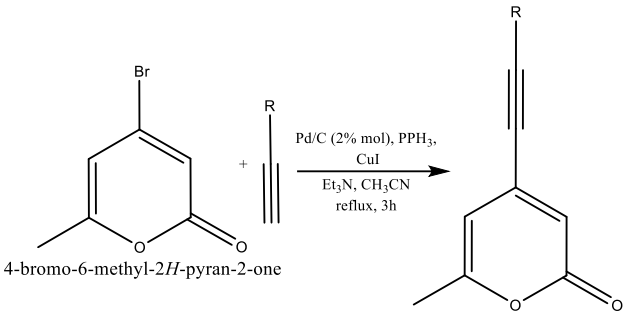
Also we have seen that 2-bromopyridine[30] is coupled with 4,4'-(pyridine-2,6-diyl)bis(2-methylbut-3-yn-2-ol) and formed 2,6-bis(6yridine-2-ylethynyl)pyridine .



In both reactions 2-hydroxy-2-propyl groups are split off by under the basic condition Grob fragmentation.

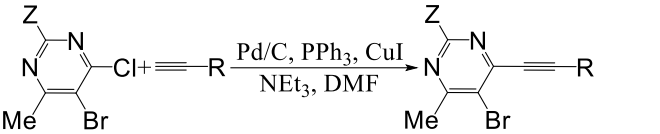
Pd/C catalysis is useful for the Sonogashira coupling reactions of pyran-2-one series[31] where bromide served as leaving group. In below table it is shown with reaction.

Sonogashira Coupling of 4-Bromo-6-methyl-2H-pyran-2-one with Alkynes Pd/C-Catalyzed[31]



No.	R	Yield(%)	No.	R	Yield (%)
1	n-Pr	72	7	4-AcNH-Ph	95
2	n-Bu	77	8	4-NO_2-Ph	95
3	n-Pen	79	9	4-Ac-Ph	35
4	Ph	74	10	CH_2OAc	0
5	CH_2OH	5	11	1-OH-cyclopentyl	61
6	CH_2OTHP	81	12	1-OH-cyclohexyl	84

In 5-bromo-4-chloropyrimidines a selective coupling in 4-position with various alkynes was observed.[32] If a second alkyne was used, remaining bromo substituents could be exchanged, Sonogashira coupling occurs.

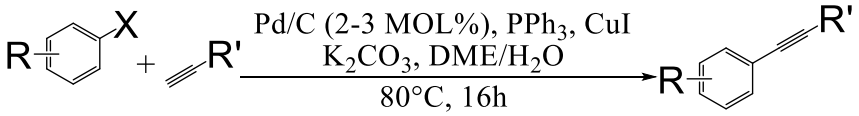


where, Z = NH_2, SEt & R = Ph, $C(Me)_2OH$, $(CH_2)_2OH$, CH(Et)(OH)

(1b) Pd on Carbon (Pd/C); In Organic Solvent/water mixtures

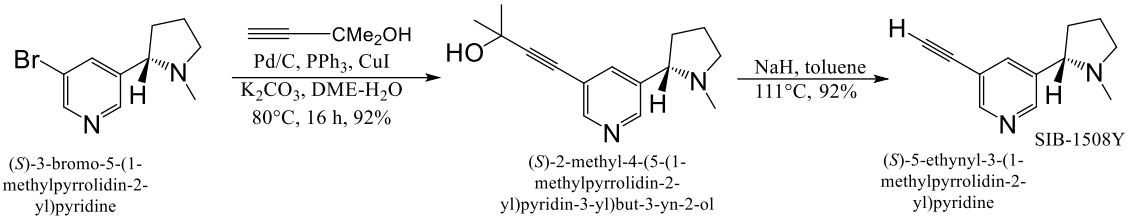
Generally, for Pd/C catalyzed Sonogashira couplings medium of here organic solvent or water mixture is useful and efficient. Here usually K_2CO_3 is used. So, aryl iodides and bromides bearing either electron withdrawing of electron donating substituents could be coupled using DME-water.[33,34]

Pd/C-Catalyzed Sonogashira Coupling of Aryl Halides with Substituted Alkynes



X	R	R'	Yield (%)	X	R	R'	Yield(%)
Br	3-CHO	CMe_2OH	98	Br	2-CN	CMe_2OH	89
Br	4-NO_2	CMe_2OH	92	I	4-OH	1-cyclohexeneyl	50
I	3-NH_2	CMe_2OH	78	I	4-CO_2H	1-cyclohexeneyl	80

Sonogashira Coupling reaction is one of the efficient process to synthesize (S)-5-ethynyl-3-(1-methyl-2-pyrrolidinyl)-pyridine (SIB-1508Y) as a novel enantiopure



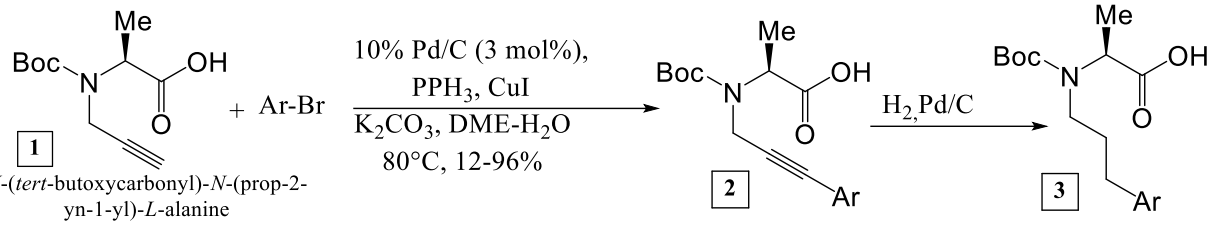
(*S*)-3-bromo-5-(1-methylpyrrolidin-2-yl)pyridine

(*S*)-2-methyl-4-(5-(1-methylpyrrolidin-2-yl)pyridin-3-yl)but-3-yn-2-ol

(*S*)-5-ethynyl-3-(1-methylpyrrolidin-2-yl)pyridine

nicotinic acetylcholine receptor agonist.[34-35,36]

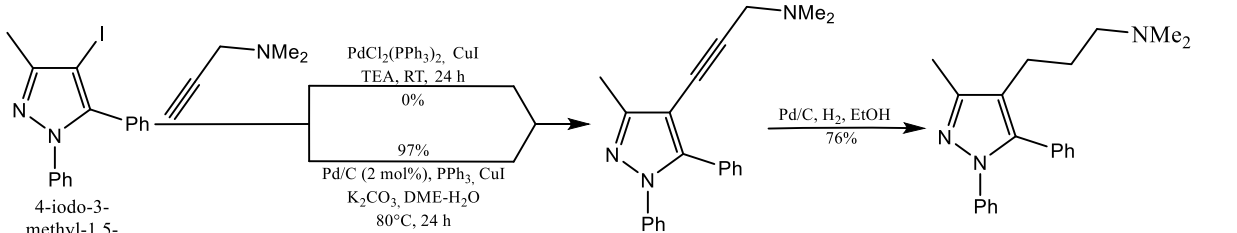
It should be remark, that using homogeneous source of Pd(0) [$Pd(PPh_3)_2Cl_2$, $Pd(PPh_3)_4$, $Pd_2(dba)_3$] were unsuccessful to synthesize the pyridine cross-coupling product. But using Pd/C-PPh_3-CuI , It's possible to coupling N-propargyl amino acids with heteroaryl or aryl bromide provides an unnatural α-amino acids, **2** then it hydrogenated to **3** .[37]



N-(*tert*-butoxycarbonyl)-*N*-(prop-2-yn-1-yl)-*L*-alanine

Here, Ar = phenyl, substituted phenyl, pyridyl, thienyl, pyrimidyl

Thereafter, Pd/C again turned more effective over homogeneous Pd(0) or Pd(II) catalysis in many cases. Such as Pd/C catalyzed Sonogashira coupling of iodopyrazole with N,N-dimethylpropargylamine.[38] Consciously, it should mention that with homogeneous catalysis with $Pd(PPh_3)_2Cl_2$ and CuI got 0% yield while Pd/C, PPh_3, and CuI provide 97% yield in this Sonogashira coupling.



4-iodo-3-methyl-1,5-diphenyl-1*H*-pyrazole

N,*N*-dimethyl-3-(3-methyl-1,5-diphenyl-1*H*-pyrazol-4-yl)prop-2-yn-1-amine

N,*N*-dimethyl-3-(3-methyl-1,5-diphenyl-1*H*-pyrazol-4-yl)propan-1-amine

In Sonogashira coupling of 4-bromo-6-methyl-2-pyrone a similar phenomenon was observed by Fairlamb et al.[39]

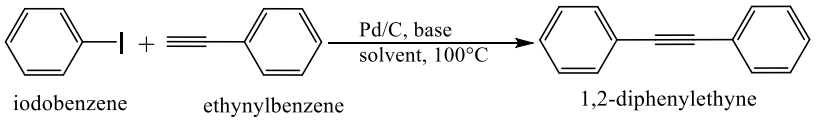
Despite of using, K_2CO_3 alternatively, diisopropylamine can be used as a base in Sonogashira coupling reaction in DMA-water medium.[27] As a solvent system alternatively, we can use water and 2-aminoethanol which also be useful.[40]

(1c) Pd on Carbon (Pd/C) Catalyzed Copper-Free and Ligand-Free Coupling

CuI and phosphine (PPh_3) ligands are applied in most of the cases of Pd/C- catalyzed Sonogashira coupling reaction but there was a success in Pd/C-catalyzed Sonogashira coupling without the addition of phosphine ligands or both CuI and phosphine ligand.

According to Köhler and co-workers, Pd/C catalyzed Sonogashira coupling of iodobenzene with phenylacetylene in absence of CuI or PPh_3.[28] After 30 minutes of using 0.125 mol% of Pd they found up to 80% yield.

Pd/C-Catalyzed Sonogashira Coupling of Iodobenzene with Phenylacetylene

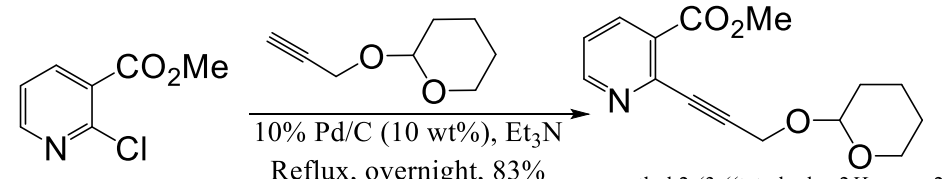


iodobenzene ethynylbenzene 1,2-diphenylethyne

	Catalyst (mol%)	Solvent	Base	time (h)	convertion rate (%)	Yield (%)
1	0.50	piperidine	piperidine	6	77	61
2	0.50	pyrrolidine	pyrrolidine	6	88	80
3	0.125	DMA	pyrrolidine	6	107	77
4	0.125	NMP	pyrrolidine	6	96	80
5	0.125	DMA	pyrrolidine	1	79	54
6	0.125	DMA	pyrrolidine	0.5	74	53

However, they found addition of CuI did not result in higher reactivity but selectivity and activity of reaction may decrease if copper is used in large quantities.

Pd/C – catalyzed Sonogashira reaction without phosophine ligand was reported by Bates & co-workers.[41] In these case, methyl 2-chloronicotinate was coupled with



methyl 2-chloronicotinate

methyl 2-(3-((tetrahydro-2*H*-pyran-2-yl)oxy)prop-1-yn-1-yl)nicotinate

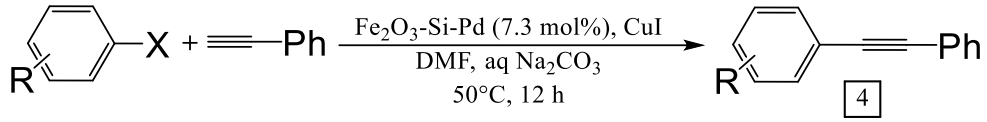
2-prop-2-ynyloxytetrahydropyran to give 83% yielded pyridyl alkyne.

In Pd/C catalyzed Sonogashira coupling, instead of applying CuI, triphenylphosphine. We can also use these conditions Pd/C (3 mol%) catalyst in DMF or DMF/water, base, KI, 130°C (in HALEX-Sonogashira reaction).[42] Then 1% Pd/C (0.2 mol%) as catalyst, i-PrOH-H_2O (1:1) and $Na_3PO_4.12H_2O$ as base at 80°C.[43]

(2) Pd on Metal Oxides as Catalyst in Sonogashira Coupling:

A magnetic maghemite (γ-Fe2O3)-silica nanoparticle supported Pd-nitrogen-heterocyclic carbene complex (Fe2O3-Si-Pd catalyst) would be used in Sonogashira reactions of aryl iodides or bromides with phenylacetylene, obtain higher yields of product [4] .[46]

Maghemite-Silica-Nanoparticle-Supported Pd-Catalyzed Sonogashira Reactions

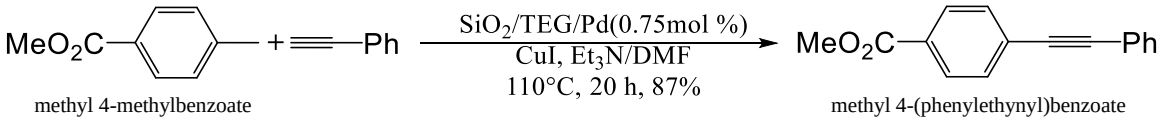


	R	X	GC Yield(%)	Isolated Yield(%)
1	2-Me	Br	94	91
2	2-Me	I	94	89
3	4-Ac	I	96	91
4	3-OMe	Br	95	93

(3) Pd on Modified Silica as Catalyst in Sonogashira Coupling:

Good catalytic activity in the Sonogashira coupling of methyl 4-iodobenzoate with phenylacetylene is shown by the catalyst obtained by encapsulation of palladium nanoparticles in a silica matrix (SiO2/TEG/Pd).[47]

SiO2/TEG/Pd-Catalyzed Sonogashira Reaction



methyl 4-methylbenzoate — methyl 4-(phenylethynyl)benzoate

Also, we got high yield of products when Pd catalyst on silica was obtained by functionalizing of 3-aminopropyl-modified silica gel with phosphine ligands and transformed into a stable immobilized palladium complex.[48] These are also applications of Cu- free Sonogashira coupling reactions.

CONCLUSIONS:

We can say that palladium on charcoal, metal oxides, modified silica are an efficient heterogenous catalyst in the Sonogashira coupling. By using these supported form of palladium, the metal contamination of the reaction mixture was very less so, we were able to reuse the catalyst (although with limited success) also we would be able to exploit the benefits of homogeneous catalysis but still retain the ease of heterogeneous catalyst separation.

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Metal or metal-containing nanoparticle @ MOF Nano composites as a promising type of photo catalyst

Project Work

Submitted for Partial Fulfilment of the B.Sc. Degree in Chemistry

By

Samir Samanta

Under the supervision of Dr. Sougata Sarkar

Samir Samanta

Reg No-A01-1112-112-022-2019

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Rahara, Kolkata - 70011

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Department of Chemistry

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Date: 13.01.22

Place: Rahara

Metal or metal-containing nanoparticle @ MOF Nano composites as a promising type of photo catalyst

ABSTRACT: Photo catalysis is a promising technology that can convert solar energy into chemical energy. However, developing photo catalysts that can be put into practice remains a major global challenge. In recent years, an emerging type of core-shell / core-shell-like composite, in which metal or metal-containing nanoparticle (M/MC NPs) cores are bound by metallic-organic structure (MOFs) shells, has attracted increasing attention to photo catalysis. These M/MC NP @ MOF Nano composites are considered to be one of the most effective and convenient ways to achieve the property combination of MOFs and M / MC NPs. Although the field is currently in its infancy, the promising results obtained have validated the potential use of M/MC NP @ MOF Nano composites in practical applications.

In this project, the basic processes of photo catalysis were briefly introduced. Synthesis of M/MC NP @ MOF Nano composites and related photo catalytic applications (e.g. photo catalytic hydrogen generation and Cr (VI) reduction) is summarized and illustrated. Special emphasis is placed on the synergistic effects between MOFs shell and NPs core which result in an enhanced performance in different photo catalyzes.

INTRODUCTION: Heterogeneous photo catalysis is considered a green technology that has been successfully used for selective biological conversion conducted under water separation, environmental remediation and ambient conditions, such as atmospheric pressure and room temperature. , Photo catalysis will play a more important role. TiO_2 in anatase form has been largely investigated for energy production and contaminant treatment due to its low production cost, high physical and chemical stability. Applications of TiO_2 have been severely hampered by growing concerns over energy and environmental band gaps (3.2 eV) and high recombination of photo generated electron-hole pairs, leading to poor energy use efficiency for solar lighting and low quantum efficiency of photo catalytic reactions. MOFs have shown great advantages for photo catalysis due to their flexible structure design and unique physical chemical properties compared to traditional photo catalysts. MOFs can strengthen their resilience against the encapsulation of M/MC NPs in the core of the shell system and prevent unwanted dissolution or corrosion during photo catalysis. MOFs can strengthen their durability against encapsulation of core encapsulation of M/MC NPs within the shell policy and avoid unwanted dissolution or erosion during photo catalysis (1) They are very high and have northern regions, which is desirable for hosting M/MC NPs; (2) MOFs can meet the specific requirements of different M/MC NPs due to the wide variety and abundance of structures and the size and shape of their tunable holes; Nano pores can provide captivity effects and shape selectivity. (3) MOFs can interact with NPs [50-52], the correct organic linkers in the structure. For M/MC NPs cores, its lower levels of Fermi energy levels (especially for noble metals) can act as reservoirs of photoelectrons and prolong the life of the photo-generated charge carrier, thus increasing overall photo catalytic performance.

SUMMARY OF THE PROJECT: Photo catalysis is a complex different catalytic process, which is controlled by many factors. Extensive investigations have been carried out to study the factors that are important for the photo catalytic process and to try to point out the mechanisms behind it. Figs.1 shows a schematic diagram of well-recognized process photo catalytic processes for semiconductors. When a given photo catalyst energy comes in contact with UV light or visible light Its corresponding band exceeds Gap Energy (e.g.), Electron (E) Events in the Valence Band (VB) will be excited by photons and spontaneously jump into the photo catalyst's conduction band (CB) and leave the same number of holes (h +) In VB, as a result Generation of photo-excited electron-hole pairs (Eq.1). The photo-generated e and h+ can then migrate to the surface of the photo catalyst, where they participate in redox reactions with adsorbed species, leading to the production of superoxide radical (O_2) (Eq. (2)) and hydroxyl radical (OH). In the case of photo catalytic degradation of organic pollutants, the pollutants (e.g., dyes, pesticides, antibiotics, etc.) can be degraded by Originated in OH VB (Eq. (5)), or directly oxidized by photo-excited h + in CB (Eq. (6)). Shown in Eq. (7), d Photo Generated e can be used for extreme reduction. Used for lyst water separation, the VB value of the photo catalyst must be below the strength of the O2 / H2O redox couple and the CB value must be above the strength of the H + / H2 redox couple [65-67]. Based on these, O2 and H2 can be produced by Eqs. (8) and (9), respectively. In the case of photo catalytic CO_2 reduction, e can only be used for specific CO_2 reduction reactions with the potential for adequate reduction (Eqs. (10-14)) [68-71], when the pores of the VB are involved in water oxidation.

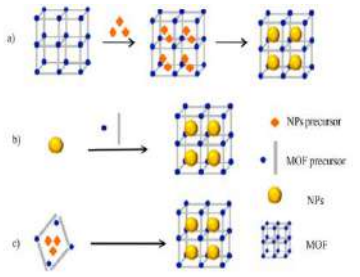


Fig. 2. Different synthetic approaches for the preparation of M/MC NPs@MOF nanocomposites: (a) the "ship-in-a-bottle" approach, (b) the "bottle-around-ship" approach, and (c) the "one-pot" approach. Reproduced with permission from Ref. [75]. Copyright 2017 MDPI.

$$\text{Catalyst} + h\nu \rightarrow \text{Catalyst}\,(e^-_{CB} + h^+_{VB}) \quad (1)$$

$$e^- + O_2 \rightarrow O_2^{\bullet -} \quad (2)$$

$$h^+ + OH^- \rightarrow {}^\bullet OH \quad (3)$$

$$h^+ + H_2O \rightarrow {}^\bullet OH + H^+ \quad (4)$$

$$\text{Dye} + {}^\bullet OH \rightarrow \text{Degradation products} \quad (5)$$

$$\text{Dye} + h^+ \rightarrow \text{Degradation products} \quad (6)$$

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O \quad (7)$$

$$2H_2O + 4h^+_{VB} \rightarrow O_2 + 4H^+ \quad (8)$$

$$2H^+ + e^- \rightarrow H_2 \quad (9)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow HCOOH,\ E_0 = -0.61\ \text{V vs NHE at pH} = 7 \quad (10)$$

$$CO_2 + 2H^+ + 2e^- \rightarrow CO + H_2O,\ E_0 = -0.53\ \text{V vs NHE at pH} = 7 \quad (11)$$

$$CO_2 + 4H^+ + 4e^- \rightarrow HCHO + H_2O,\ E_0 = -0.48\ \text{V vs NHE at pH} = 7 \quad (12)$$

$$CO_2 + 6H^+ + 6e^- \rightarrow CH_3OH + H_2O,\ E_0 = -0.38\ \text{V vs NHE at pH} = 7 \quad (13)$$

$$CO_2 + 8H^+ + 8e^- \rightarrow CH_4 + 2H_2O,\ E_0 = -0.24\ \text{V vs NHE at pH} = 7 \quad (14)$$

THE SYNTHETIC STRATEGIES OF M/MC NP@MOF NANOCOMPOSITES:

In general, preparation of M/MC NP @ MOF Nano composite can be classified into four methods, which were presented Figure 2 [75]. The first method is to introduce MOFs in one of the solution follows the previous M / MC NPs Formation of M / MC NPs inside MOFs (Figure 2a). This

The method is also called "ship-in-a-bottle" method, which M / MC is expected to limit the growth of NPs and prevent them Frozen. Particle formation is subsequently triggered in MOFs through the application of reducing agents, heat or radiation [46]. Using this method, metallic and bimetallic NPs including Rh, Ni, Pt, Pd, CuCo, AuCo and AuNi have been successfully made; immobilized inside the hole without different types of MOFs.

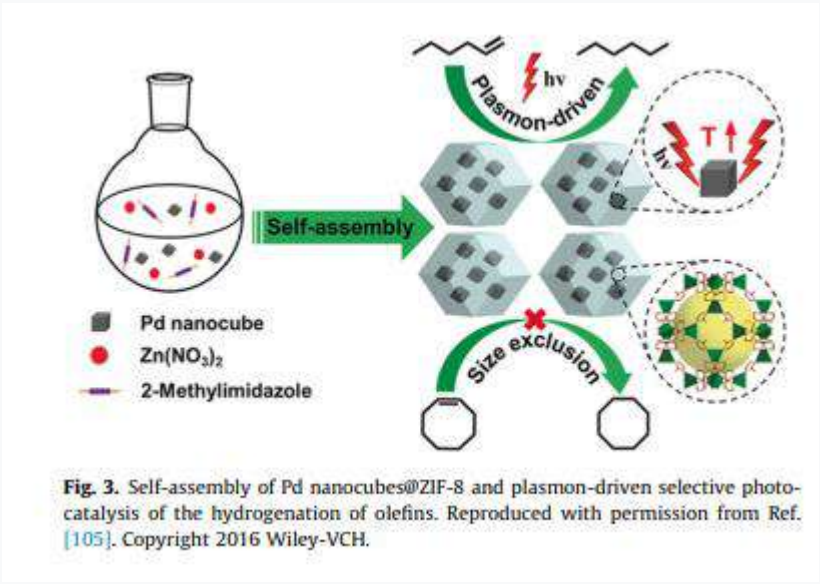


Fig. 3. Self-assembly of Pd nanocubes@ZIF-8 and plasmon-driven selective photocatalysis of the hydrogenation of olefins. Reproduced with permission from Ref. [105]. Copyright 2016 Wiley-VCH.

Metal NP @ MOF for photo catalysis: Metal NPs (M NPs), especially noble metal NPs, have attracted intense attention to heterogeneous catalysts [79-82]. Unfortunately, there are a number of unavoidable reasons associated with these NPs For example; they reduce the tendency for thermodynamically unstable and continuous catalytic reactions to converge. Surface strength [83-87] as a result,

dispersion control M NPs are high in resolution and an important factor for achievement Stable activity. A new method to improve the catalyst performance of an M NPs catalyst, the catalyst is built into a core-shell architecture, consisting of the inner core (M NPs) is bound by perforated shell material [51,98,99]. Over the years, a variety of MNP @ perforated components Polymers [100], metallic oxides [101,102], carbon [103], silica [104] and MOFs [98]. In 2016, Yang et al. [105] rationally designed and fabricated Pd nanocubes @ ZIF-8 composites through a self-assembled method (Fig. 3), and applied them to selective catalytic hydrogenation of olefins under visible light irradiation in the MOFs shell. In 2016, Li et al. [112] reported the encapsulation of Pd Nano clusters inside the cage of NH2-UiO-66(Zr) via a double-solvent approach combined with a photo reduction process (Fig. 4a). By successful coupling of the Pd catalysis with MOF-based photo catalysis, the as-prepared Pd @ NH2-UiO-66(Zr) showed excellent performance for Suzuki coupling reaction under visible-light irradiations.

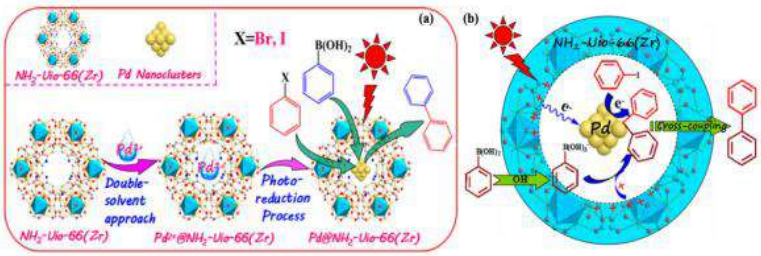


Fig. 4. (a) Schematic illustration of the preparation procedures for Pd@NH_2-UiO-66(Zr); (b) proposed mechanism of the visible-light promoted Suzuki coupling reaction over Pd@NH_2-UiO-66(Zr). Reproduced with permission from Ref. [112]. Copyright 2016 American Chemical Society.

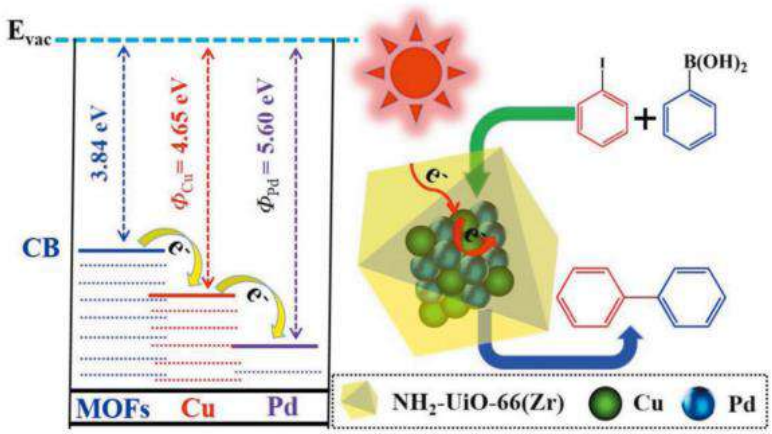
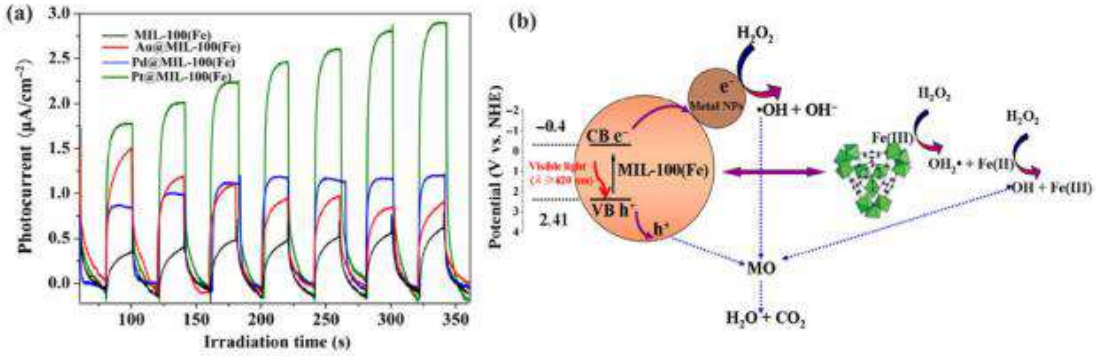


Fig. 5. Cu-mediated electron transfer process over CuPd@NH_2-UiO-66(Zr) for enhanced light-induced Suzuki coupling reaction. Reproduced with permission from Ref. [115]. Copyright 2018 Wiley-VCH



Metal oxide NP @ MOF for photo catalysis: Metal oxide catalysts have appeared as essential in most catalytic reactions performed industrially [132–134]. Among various metal oxides with semiconducting properties, TiO_2, ZnO, and Fe_3O_4 have received a lot of attention in photo catalysis. TiO_2, with a band gap of 3.2 eV, is the most used and classical photo catalytic material.

<u>TiO_2 NP @ MOF</u>: TiO_2, a widely studied semiconducting photo catalyst, has attracted tremendous attention in the past decades [144–146]. However, it remains challenging to the large-scale industrial application of pure TiO2 [147–149]. The combination of MOFs and TiO2 provides a great opportunity for the construction of new photo catalysts [150].

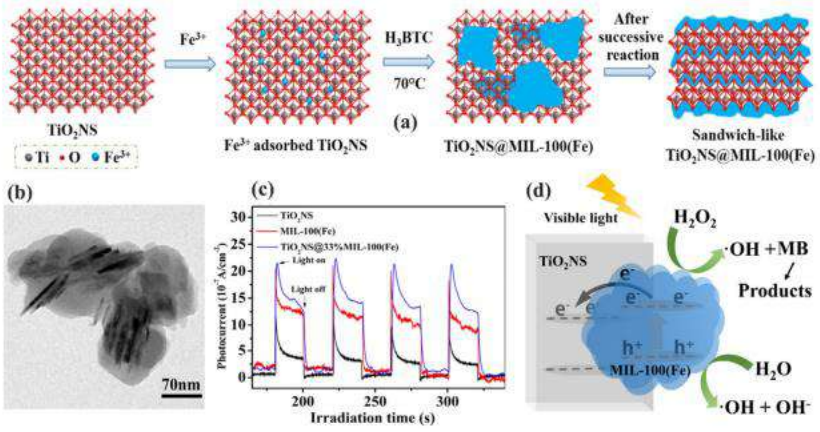


Fig. 9. (a) Synthetic illustration of the preparation procedures for TiO_2NS@MIL-100(Fe). (b) TEM images of the as-synthesized TiO_2NS@MIL-100(Fe). (c) Transient photocurrent response of MIL-100(Fe), TiO_2NS, and TiO_2NS@MIL-100(Fe) in 0.2 M Na_2SO_4 solution under intermittent visible light irradiation (≥420 nm). (d) Proposed mechanism for photocatalytic generation of ·OH over TiO_2@MIL-100(Fe). Reproduced with permission from Ref. [156]. Copyright 2017 Elsevier.

<u>ZnO NP @ MOF</u>: In 2013, Zhan et al. [162] successfully synthesized the freestanding ZnO @ ZIF-8 Nano rods by a simple self-template strategy for the first time. As shown in Fig. 10A, ZnO Nano rods not only provide Zn^{2+} ions but also act as the template for the formation of ZIF8. The TEM images (Fig. 10B) clearly demonstrate that ZnO @ ZIF-8 Nano rods with the thickness of the outer shell about 300 ± 25 nm have been successfully prepared , the obtained ZnO @ ZIF-8 Nano rod arrays exhibited a good photo electrochemical response to H_2O_2 (the scavenger). Meanwhile, the photo generated e can be transferred to the electrode substrate, leading to a remarkable enhancement in the photocurrent response of ZnO Nano rods. Several research groups have successfully synthesized ZnO @ MOF core – shell heterostructures and demonstrated their high catalytic activity for pollutants treatment [167,168], water splitting [169], and liquid hydrogenation [170]. It was suggested that under the light irradiation, e could be more easily excited from the VB to the CB of MOFs in the ZnO @ MOF composites [169]. These photo-excited e in the CB of

MOFs would be quickly transferred to that of ZnO. In the meantime, the photo generated h+ on the VB of ZnO can be transferred to the VB of MOFs shell [171]. The above processes result in more effective separation of photo-excited electron-hole pairs and can thus suppress their recombination [167,169]

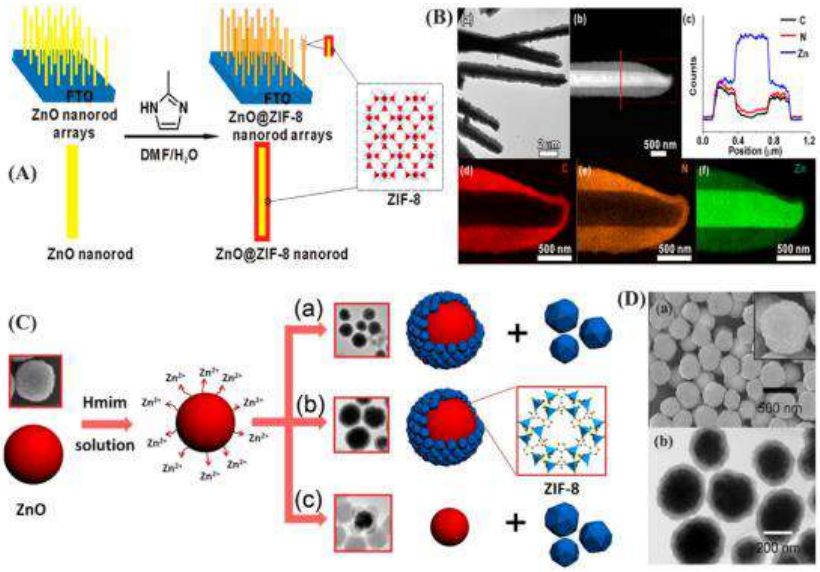


Fig. 10. (A) Schematic illustration of the preparation procedures for ZnO@ZIF-8 nanorods. (B) (a) Low-magnification TEM image of ZnO@ZIF-8 nanorods; (b) high-magnification TEM image of an individual ZnO@ZIF-8 nanorod; (c) the cross-sectional compositional line (marked in panel b) profiles of ZnO/ZIF-8; (d–f) the corresponding elemental maps of C, N, and Zn in the ZnO@ZIF-8 nanorod. Reproduced with permission from Ref. [162]. Copyright 2013 American Chemical Society. (C) Schematic illustration of structures obtained using different concentrations of Hmim (a) 4.51 M, (b) 3.66 M, and (c) 1.83 M. (D) SEM (a) and (b) Tem images of ZnO@ZIF-8 heterostructures.

<u>CONCLUSION</u>: In this project I have summarized and exemplified the synthesis of M/MC NP @ MOF core–shell and core–shell like Nano composites s and their applications in heterogeneous photo catalysis, which includes photo catalytic water-splitting, Cr(VI) reduction, CO_2 reduction, non-selective processes for the degradation of pollutants and selective organic transformations to fine chemicals

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Sillica-supported palladium: Sustainable catalyst for cross-coupling reactions

Project Work

SUBMITTED FOR Partial Fulfillment of the B.Sc Degree in Chemistry

By

Samir Sarkar

Under the supervision of Dr. Buddhadeb Dutta

Registration No. : A01-1112-112-048-2019

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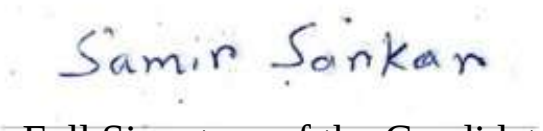

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Sillica-supported palladium: Sustainable catalyst for cross-coupling reactions

❖ Abstract:

Cross- coupling reactions is a typochemical reaction that allows to form sp2-sp2 bonds by Palladium catalyst or palladium supported on solid support like silica, carbon. Heterogeneous palladium catalyst is the most used catalyst for the cross-coupling reactions. Over the last 40 years C-C bond forming reactions have gained immense importance for their use in biological and pharmaceutical important organic fragments. The majority of the heterogeneous catalyst are based on silica supported because silica shows some advantageous properties like chemical stability, thermal stability.

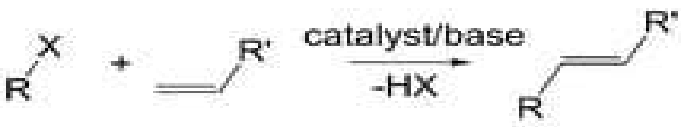
❖ Introduction

In the transition series palladium is the most used transition metal for cross-coupling reactions. Cross-coupling reactions (Heck, Suzuki,sonogashira) synthesised many valuable product for the industrial and fine chemistry. The uses of catalyst increase due to high activity, selectivity to the target products and they also have to easily accessible, stable and recyclable. Solid supported palladium catalyst used more than homogeneous catalyst for the cross-coupling reactions. Palladium can be deposited on a solid support in different ways. We can deposited palladium catalyst over different types of silica like amorphous silica, mesoporous molecular sieves. This work provides an overview of the chemistry of silica-supported palladium catalysts advantages and limitations of various supports and immobilised ligands.

❖ Sillica-supported palladium catalyst for carbon-carbon bond formation:

❑ Heck Reaction

The Heck reaction, discovered by Tsutomu Mizoroki and Richard F. Heck. Heck reaction is the chemical reaction of an unsaturated halide with an alkene in the presence of a base and a palladium catalyst to form a substituted alkene. This is the suitable example of C-C bond forming by cross-coupling reaction. One of the benefits of the Heck reaction is its outstanding trans selectivity . The reaction proceed through relatively mild condition and it affords highyields of the desired product. The Heck reaction used in polymer synthesis. One of the major drawbacks of the Heck reaction is precipitation of the palladium catalyst (black color) that prevent the activity of the active species .So consequently numerous attempts have been made to prevent these precipitation by a solid support like silica . The general form of the Heck reaction is [4]

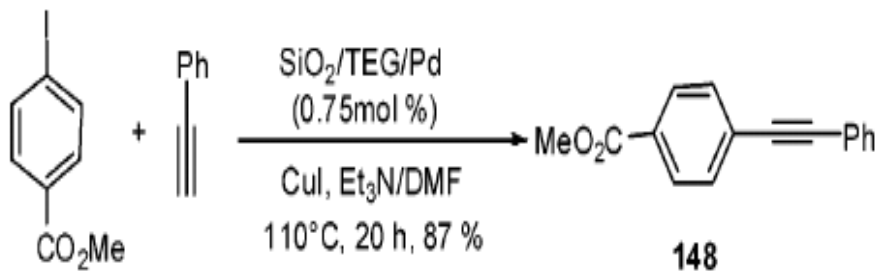


R = Ar, Bn, vinyl
R' = H, Alk, Ar, COOAlk
X = Cl, Br, I, OTf

Silica supported palladium catalyst highly active in C-C coupling reaction. The reactivity of the different aryl halides decreases from iodide to bromide and chlorides due to different strength of aryl-X bond (C-I < C-Br < C-Cl).

❑ Sonogashira Reaction

Sonogashira reaction is a sp2-sp cross-coupling reaction between terminal alkene and an aryl or vinyl halide (in presence of palladium catalyst). It is the most preferred method for the preparation of the conjugate enynes and arylalkyles . The reaction can be carried out under mild condition , such as at room temperature, in aqueous media, and with a mild base which has allowed fot the use of the Sonogashira cross-coupling reaction in the synthesis of the complex molecules. We can see that if we use palladium supported in silica catalyst in the sonogashira reaction of terminal alkynes with aromatic halides we get yields of the coupling products. This reaction used in organic synthesis to form carbon-carbon bonds . The silica supported palladium showed high catalytic activity in the sonogashira reaction. The catalyst obtained by encapsulation of palladium nanoparticles in a silica matrix(SiO2/TEG/Pd) showed high catalytic activity in the sonogashira coupling of methyl 4-iodobenzoate with phenyl acetylene

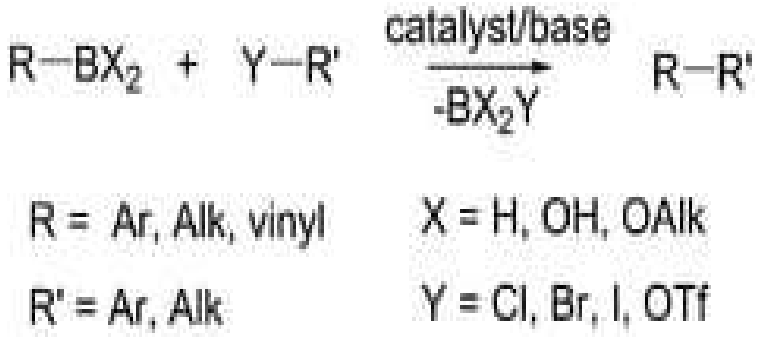


scheme 1 [5]

Specific example include its use in the synthesis of Tozarotne[1], which is a treatment for psoriasis and acne and in the preparation of SIB-1508Y, also known as Altinicline[2] , a nicotinic receptor agonist.

❑ Suzuki-Miyaura reactions:

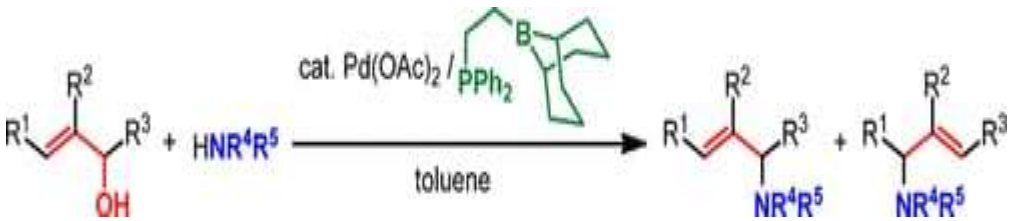
The Suzuki-Miyaura reaction is a part of coupling reaction also known as Suzuki reaction. The Suzuki reaction is currently most used and the most efficient in medicinal chemistry . It is a metal catalyzed reaction, typically with palladium . In the Suzuki coupling reaction the coupling partners are a boronic acid and an organo halide and an catalyst. It is one of the most versatile and frequently employed method for carbon-carbon bond formation. Homogeneous palladium complexes possess high activity for the cross-coupling reaction. If we use homogeneous catalyst for the reaction it is difficult to separate the product from the catalyst and reusing the catalyst . To overcome the difficulty homogeneous palladium catalyst have been attached to various supports like mesoporous silicas. Using supported palladium catalyst(like silica) for Suzuki-Miyaura cross-coupling reaction is a heterogeneous catalysis .During the reaction palladium could be release from the surface of the solid support and this released palladium could be responsible for the catalysis as a homogeneous mechanism.General form of the Suzuki-Miyaura equation [4]



❖ Silica-supported palladium catalysts for carbon–nitrogen bond formation

❑ Amination of allylic compounds:

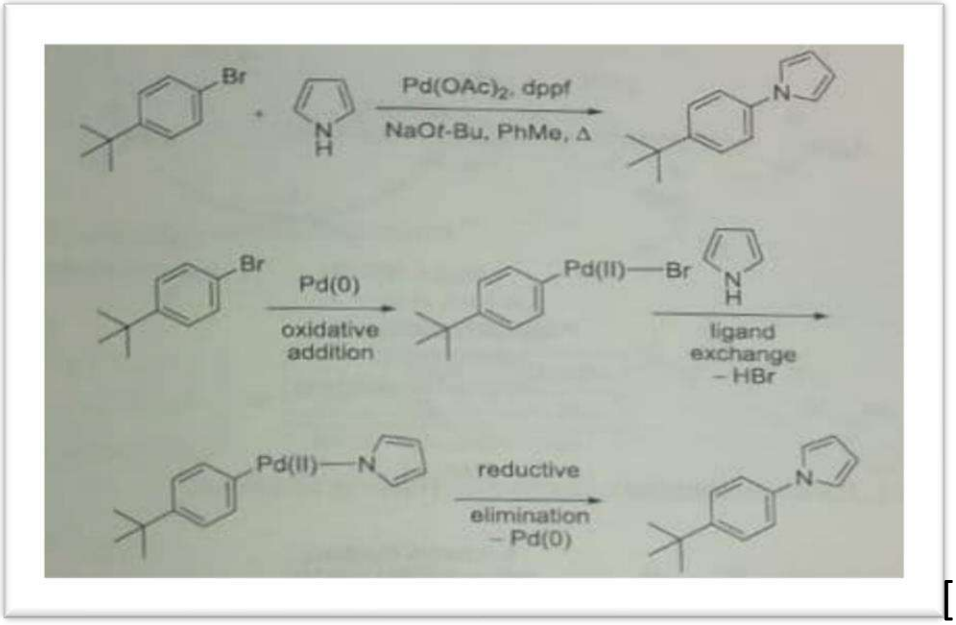
Amination is the process by which an amine group is introduced into an organic compounds. Amination is a C-N bond formation process. Pd catalyst is used for the amination of the allylic compounds like allylic alcohols/ester with secondary amines in short reaction time at room temperature . A number of homogeneous chiral ligand have been developed for these kind of reactions. For the amination of arryl substituted allylic alcohols, complex of palladium catalyst and a ligand L (Bis phosphine ligand) was used so that we get an good yield. For the amination of ketone or aldehyde, ketone and aldehyde can be converted to amines through catalytic or chemical reduction in the presence of ammonia or an amine . Primary ,secondary and tertiary amine can be prepared this way.



Amination of a secondary alcohol [6]

❑ Buchwald-Hartwig reaction

Buchwald-Hartwig reaction is a chemical reaction used in organic chemistry for the synthesis of carbon nitrogen bonds via the palladium catalyzed coupling reaction. This reaction widely used in synthetic organic chemistry . This reaction is applied in many total synthesis and the industrial preparation of numerous pharmacuticals . By this reaction arylamine or heteroaryl like pyridineamines are formed by the reaction of an arylhalides or triflate with a primay or secondary in the presence of Pd catalyst .



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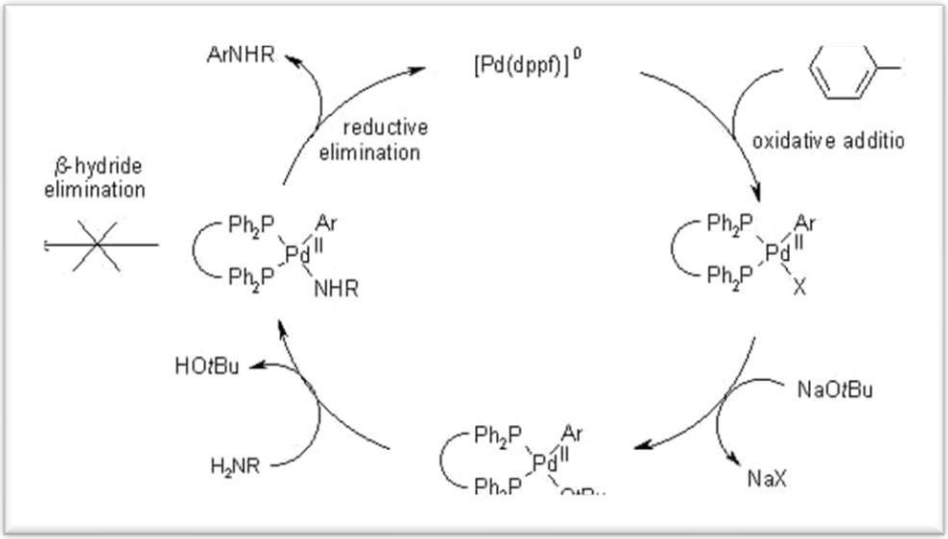

❖ Conclusions:

We know about the numerous uses of Pd silica supported catalysts and the use ofit progressing day by day in modern chemistry .There are many advantages in using silica supported catalysts ,such as easyly available, excellent stability, easy separation from the reaction mixture ,reusability for several times with often minimal loss of activity etc.Though there are numerous advantages there are many drawbacks in using this catalyst , such as the mechanism of most of the coupling reactions is still unclear . In addition, the heterogeneous catalyst sometimes can require higher reaction temperature and catalyst loadings and has limitations in stereoselective reactions. In future there will be many discoveries to get far better procedures to use these catalysts .

❖ References:

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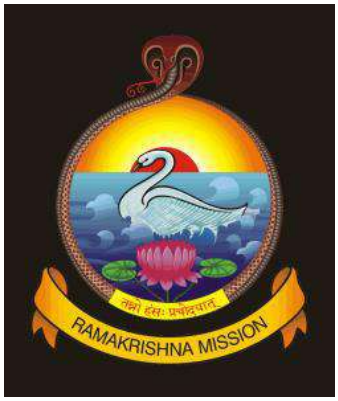
RECENT DEVELOPEMENT ON FLUORESCENT BASED CHEMOSENSORS

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

Santu Dhal



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I gratefully acknowledge our respected Principal Maharaj for giving inspiration and motivation.

I am grateful to my advisor, Dr.Debabrata Jana, Department of Chemistry, Ramakrishna Mission Vivekananda Centenary College, Kolkata-700118 for his guidance on the related area of this project work and continuous support.

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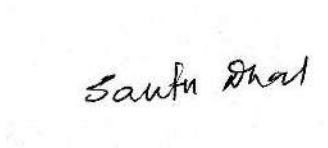

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RECENT DEVELOPEMENT ON FLUORESCENT BASED CHEMOSENSORS

ABSTRACT

Fluorescent chemosensors have been widely applied in many diverse fields such as biology, physiology, pharmacology, and environmental sciences for the detection of biologically and/or environmentally important species. The field of fluorescent chemosensors is being developed for about 150 years. Since then a wide range of chemosensors had been discovered. Despite the progress made in this field, several problems and challenges still exist. This review article provides a general overview of the development in the research of fluorescent sensors. The application of chemosensors in various established and emerging biotechnologies is very bright.

Keywords: Supramolecular Chemistry, Biosensors, Chemosensors, Bioimaging.

INTRODUCTION

Chemosensors are molecular structures that are used for sensing an analyte. When it binds with a specific ion or molecule it produces an observable change that signals the presence of that particular ion or molecule. Fluorescent chemosensors are consisted with a fluorophore part and a binding site. If the binding sites operate via irreversible chemical reactions then the indicators are described as fluorescent chemodosimeters.

The first fluorescent chemosensor was reported by F. Goppelsro¨der in 1867. It was used for the determination of aluminum ion (Al^{3+}) through the formation of a strongly fluorescent morin chelate. Since then a number of fluorescent chemosensors have been developed for the determination of many other metal ions. In this short review we are going to present the subsequent development of chemosensors and their uses in various biological and analytical processes.

At the very beginning, chemosensors were used to detect only metal cation rather than anions and neutral species. This is because these compounds can easily bind metal ions in water. Around 1980, de Silva and Czarnik who are regarded as two fathers of modern chemosensors, pioneered the growth in the development of fluorescent chemosensors. Since those pioneering days, an extensive development of fluorescent chemosensors as well as the scope of their applicability in numerous biological fields, have been extended.

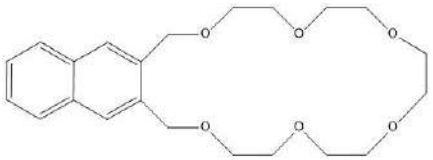
National status: In the last decade huge development has been done by the Indian scientist in the field of chemosensors. Detection of toxic metal ions or bio-molecules is one of the most challenging research fields today. Prof. K. Ghosh and his co-workers designed and synthesized new type of chemosensors for sensing of cations, anions, neutral molecules. Prof. Moorthy and co-workers have significant contribution in the field of supramolecular chemistry and published huge number of research work in the international journel. Prof. Ramanathan and his co-workers performed various research works on the development of fluorescence probes for binding specifically different biological molecules. Prof. N. Parveen and co-workers also carried out evolutionary work in the field of fluorescence imaging using water soluble small molecules. Prof. Chowdhury and his co-workers have significant contribution in the field of Single fluorescence Sensor in solid state using polymer–thin film. The dignified work on the field of fluorescence sensing of biophysically relevant analysis has been improved by of Prof. A. Dutta and his co-workers. Prof. R. Anand and co-workers have also sincere work in the field of biosensors for detecting organic pollutants and process for producing the same. Prof. T. Majumdar and his co-workers have done extensive research work on the field spectroscopic and computational studies of some optical sensors of metal ion and anion. Prof. A. K. Mahapatra and his co-workers carried out versatile research work on the field of Chemosensors, Chemodosimeter and Supramolecular chemistry. This group developed novel small molecules for sensing of metals ions in solution phase.

DISCUSSION:

Fluorescent chemosensors for cations: Human body and the environment contains large number of metal ions among them some are essential for our life such as sodium (Na^+) potassium (K^+), calcium (Ca^{2+}), copper (Cu^+ and Cu^{2+}) and zinc (Zn^{2+}) and some are toxic and hazardous such as lead (Pb^{2+}), cadmium (Cd^{2+}) and mercury (Hg^{2+}). To detect these metal ions selectively, a number of chemosensors have been developed.

Fluorescent chemosensors for alkali and alkaline earth metal ions: The mechanism of binding of metals by fluorescent chemosensors involves coordination interactions between the hosts and the guest .Two naphthalene based chemosensors are shown in (Fig 1) i.e. **1** and **2** which also exhibit dichotomous behaviour. It was observed that when 1 formed a complex with alkali metal chloride salts in 95% ethanol glass at 77 K it displayed a decrease in fluorescence quantum yield, also an increase in phosphorescence quantum yield, and a slight decrease in phosphorescence lifetime but for the complexation of **2** with potassium (K^+), rubidium (Rb^+),

or caesium (Cs^+) chloride salts caused a noticeable increase in fluorescence quantum yield, also a decrease in phosphorescence quantum yield, and a substantial decrease in phosphorescence lifetime. The reason behind these changes are the heavy atom effect (for Rb^+ and Cs^+), complexation induced change in triplet energy relative to the ground and excited singlet state energies as well as rigidification and conformational effects.



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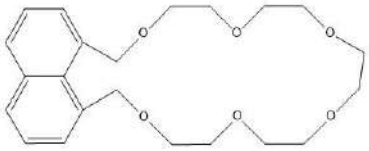

2

Fig.1: Structures of the fluorescent chemosensors **1, 2**.

Fluorescent chemosensors for d-block metal ions:

The uses of chemosensors is not only limited for the detection of alkali metal and alkaline earth metal ions but also they are used to capture the transition metals since these metals take part in various chemical reactions.

Copper (Cu), the third most abundant transition metal in the human body, is involved in various physiological and pathological processes. Imbalance of copper causes diseases like Menkes (copper deficiency), Wilson's (copper overload), Alzheimer's disease, prion disorders, neurodegeneration and cancer.

In 1997, Czarnik and co-workers developed a rhodamine-B derivative and its ring-opening reaction for sensing copper ion (Cu^{2+}).

Fluorescent chemosensors for anions:

Anions play an important role in biological and industrial processes also the environment contains a number of anionic pollutants. There are a number of fluorescent chemosensors have been developed for the detection of anions have used host–guest interactions or chemical reactions, over the past several decades. The mechanism through which they bind with ions may be a guest host interaction or may be a chemical reaction.

Fluorescent chemosensors for small neutral molecules: We have various neutral molecules in environment .While small neutral molecules such as reactive sulfur species (RSS) and some

neutral ROS/RNS are essential for our survival, some small neutral molecules like nitroaromatics (explosives), and nerve-gas are a threat to health. These two important reasons have stimulated the development of fluorescent chemosensors for small neutral molecules over recent years.

Fluorescent chemosensors for reactive sulfur species (RSS): Intracellular thiols such as cysteine (Cys), homocysteine (Hcy) and glutathione (GSH) have vital roles in biological systems. Abnormal levels of these molecules can cause a number of diseases, such as liver damage, leucocyte loss, psoriasis, cancer and AIDS. That is why the detection of these thiolcontaining biomolecules in biological samples has become very important. The first use of PET sensors for thiols was demonstrated by de Silva in 1998. In 2004, two squaraine based fluorescent chemosensors 33a and 33b (Fig.2) was developed for the detection of thiols by Martı´nez-Ma´n˜ez and co-workers. Due to the selective addition of thiols to the cyclobutene ring in the chemosensors these solutions showed colour changes from blue to colorless in the presence of thiol-containing compounds. These thiol chemosensors cannot distinguish Cys/Hcy and GSH.

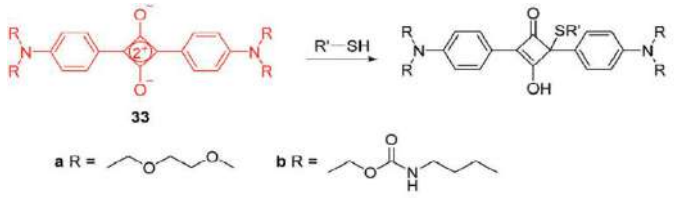

Fig. 2: Structures and proposed mechanism of **33 (a)** and **(b)** for detection of thiols.

Fluorescent chemosensors for biomacromolecules:

In living biological systems biomacromolecules play a vital role. However, the abnormal function of these biomacromolecules often has huge impact on living bodies. The fluorescence imaging techniques is a powerful tool for studying these biomacromolecules and to fully understand their purpose in these complex biological systems. The chemosensors show excellent spatial and temporal resolution and high molecular specificity with these biomolecules. The detection of biomacromolecules is not an easy task as they often have large molecular weights, complex structures and a range of biological functions. Over the past several decades, a number of fluorescent chemosensors have been developed, which have proven to be a must for bioimaging and used in the investigation of diseases.

Czarnik carried out pioneering work on anthrylpolyamine based chemosensors to sense polyanions such as heparin, poly-L-glutamate, ds DNA (double-stranded DNA) and ss DNA (single-stranded DNA) in water. These chemosensors display a redshift and a decrease in their emission spectra when they bound to either ds DNA or to ss DNA.

A pyrene-based peptide beacon (fluorescent chemosensor 46) has been reported by Schmuck and co-workers. It was shown to intercalate with DNA (Fig.3). While the folded conformation of 46 exhibits a typical pyrene excimer emission in solution, it undergoes a conformational change to the unfolded form when bound to DNA. During the change in conformation, a ratiometric change in fluorescence from excimer (490 nm) to monomer emission (406 nm) is observed.

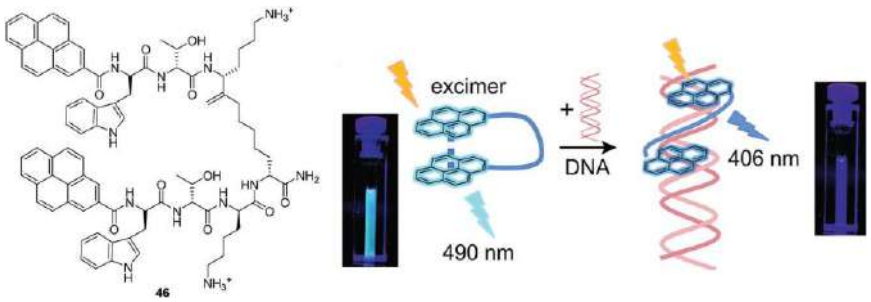

Fig.3: Structures of the fluorescent chemosensors **46** and the schematic illustration of **46** and Its Interaction with nucleic acid (the photographs show the corresponding cuvettes under UV light).

CONCLUSION

Over the past 50 years the field of fluorescent chemosensors has been developed explosively. The growth in this vast field is deeply pioneered by the research of Professor Anthony W. Czarnik's and Professor A. Prasanna de Silva. Within a very short time the field is flourished and is recognised as a branch of chemistry. Research workers expect that the field of chemosensors will continue to expand. To meet new challenges we need increasing number of new and improved chemosensors as well as we have to find new approaches or applications of existing fluorophores.

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Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit

Project Work

Submitted for partial fullfillment of the B.Sc. Degree in Chemistry

By

Satadru Dutta

Under the supervision of Dr. Bipul Mondal

Satadru Dutta

Reg. No.- A01-1112-112-019-2019

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Date: 15/01/2022

Place: Rahara

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RAHARA, KOLKATA – 700118

To Whom it may concern

This is to certify that the project entitled "Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit" is the result of review work done by Mr. Satadru Dutta, who has registered his name in "Ramakrishna Mission Vivekananda Centenary College (Autonomous), Rahara, Kolkata-700118, in undergraduate level. This work has been carried out under my supervision in this college.

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Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit

ABSTRACT

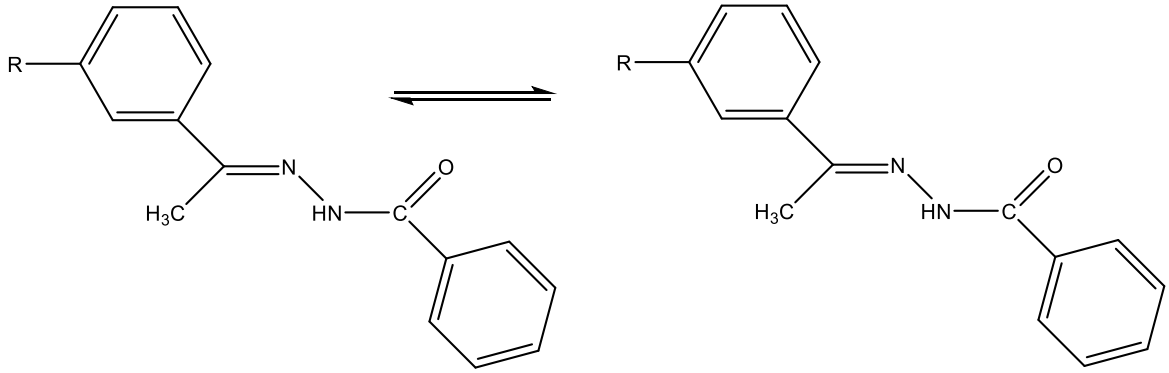
Dinuclear trioxidic [$(VOL)_2\mu$-O] (1-4) complexes were synthesized from the reaction of [$VO(acac)_2$] with an equimolar amount of H_2L [H_2L is the general abbreviation of hydrazone ligands (H_2L^{1-4}) in which the two H's representing the dissociable phenolic and amide protons, derived from the condensation of benzoyl hydrazine with either 2-hydroxyacetophenone or its para substituted derivatives] in acetone or dichloromethane or acetonitrile. These $V_2O_3L_2$ complexes were also obtained from the reaction of $VOSO_4$ with H_2L in the presence of two equivalents sodium acetate in aqueous-methanolic (50% V/V) medium and also from the decomposition of [$V^{IV}O(L)$(bipy/phen)] complexes in CH_2Cl_2 solution. Black monoclinic crystals of 2 and 4 with C2/c space groups were obtained from the reaction of [$VO(acac)_2$], respectively with H_2L^2 and H_2L^4 in acetone in which the respective ligands are bonded meridionally to vanadium in their fully deprotonated enol forms.

These dinuclear complexes are converted to the corresponding mononuclear cis *dioxido* complexes $K(H_2O)^+[VO_2(L)]^-$ (5-8) and mixed ligand [VO(L)(hq)] complexes on rection with 2 equivalent KOH in methanol and 2 equivalents 8-hydroxyquinoline in chloroform. Ascorbic acid reduces the dioxovanadium(V) complexes reversively under aerobic condition.

INTRODUCTION

Vanadium is an interesting transition element is relatively abundant (~ 0.015% of earth's crust) in nature and is present in plant and animal cells [1] at concentration 10-20 nM. Among the wide range of possible oxidation state -III to +V, Vanadium easily switches between +IV and +V and the stabilization of either of these two states under aerobic condition depends upon the basicity of the coordinated ligand and also on the pH of the reaction medium. The +V state has received considerable attention probably due to its two important properties: (i) it can exist in three motifs *viz*., mononuclear VO^{3+} and VO_2^+ motifs and dinuclear $V_2O_3^{4+}$ motif and (ii) it could exist in either 5 or 6 coordinated environment. These motifs are stable in solution around the physiological pH(~7) only when the metal is coordinated with sufficiently strong ligand for preventing the precipitation of hydroxides. The objectives of this review: (i) to synthesize the complexes containing $V_2O_3^{4+}$ core with a family of hydrazone

ligands, (ii) To study the various synthetic routes for the formation of such type of complexes, (iii) To examine the feasibility of conversion of these dinuclear complexes into the mononuclear complexes with VO^{3+} and VO_2^+ motifs and (iv) to study the electronic effect of para substituents in the hydrazone ligands on the vanadium in these complexes. Here the four tridentate dibasic hydrazone ligands H_2L^{1-4}, have been used, derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone and its para-substituted derivatives.



R	H_2L
H	H_2L^1
CH_3	H_2L^2
OCH_3	H_2L^3
Cl	H_2L^4

Fig. 1

SUMMARY OF THE PROJECT WORK

Synthesis of H_2L^{1-4}

These hydrazone ligands derived by the condensation of benzoyl hydrazine with 2-hydroxyacetophenone and its 5-substituted derivative [2,3] in methanol. In the free state, these are present in their keto-form but they undergo complexation through their completely enol form as indicated by their IR and ^1H NMR spectra.

Synthesis of the complexes $[V_2O_3L_2]$ (1-4)

All dinuclear trioxide $[V_2O_3L_2]$ complexes were synthesized by different methods using various starting materials, *viz*., (i) equimolar amount of $[V^{IV}O(acac)_2]$ and H_2L under refluxing condition in non-hydroxylic solvent [3] e.g., acetone, CH_2Cl_2, acetonitrile etc.; (ii) by reacting $VOSO_4$ with equimolar amount of H_2L in presence of two equivalents sodium acetate in aqueous-methanolic medium [3] and (iii) by the decomposition [4] of $[V^{IV}O(L)(bipy/phen)]$ complexes in non-hydroxylic solvent like CH_2Cl_2, $CHCl_3$, C_6H_6 etc. In

all the above methods the starting materials are different tetravalent precursors, and the oxidizing agent is most likely the aerial dioxygen. These reactions are represented by the following equations 1, 2, 3:

$2[V^{IV}O(acac)_2] + 2H_2L + ½O_2 \rightarrow [V^{V}_2O_3L_2] + 4Hacac$ - - - - - - - - - - (1)

$2VOSO_4 + 2H_2L + 4CH_3COONa + ½O_2 \rightarrow$

$[V^{V}_2O_3L_2] + 2Na_2SO_4 + 4CH_3COOH$ - - - (2)

$2[V^{IV}OL(bipy/phen)] + ½O_2 \rightarrow [V^{V}_2O_3L_2] + 2(bipy/phen)$ - - - - - - - -- (3)

Where Hacac, bipy and phen are representing respectively acetylacetone, 2,2′-bipyridine and 1,10-phenanthroline.

Monoclinic crystals of $[V_2O_3(L^2)_2]$ (Fig. 2) and $[V_2O_3(L^4)_2]$ (Fig. 3) with *C2/c* space group were obtained by following the above-mentioned preparative method (1), while orthorhombic crystals of $[V_2O_3(L^2)_2]$ (Fig. 4) with *Pbca* space group were obtained by adopting the preparative method (3). The analytical, spectral (IR, UV-vis and 1H NMR) and electrochemical data of these two dimorphs are identical (within experimental error). The solid-state structural features of these dimorphs differ in crystal packing and in the molecular symmetry. In the monoclinic variety, two structurally very similar but crystallographically distinct respective molecules are present in both the crystal lattices of $[V_2O_3(L^2)_2]$ and $[V_2O_3(L^4)_2]$ with the bridging oxygen lying on a crystallographic 2-fold axis such that the two halves of each of the two molecules are crystallographically equivalent while in the orthorhombic variety of $[V_2O_3(L^2)_2]$, discrete molecules constitute the crystal lattice and the bridging atom has no crystallographic symmetry but two halves of the molecule have closely matching dimensions. However, in both varieties the geometry at metal center is a distorted square-pyramid with the meridionally disposed respective hydrazone ligand in enol form. The bridging oxo-oxygen occupies the fourth position of the square plane and the terminal oxo-oxygen is occupied in one of the two axial positions. The two terminal oxygen atoms O(1) and O(1)$1 (for the crystals with *C2/c* space group) or O(1) and O(1a) (for the crystals with *Pbca* space group) are mutually *trans* lying on opposite sides of the V−O−V plane. The extent of distortion is different for each of the vanadium centers even within the same structure. The V-O bond lengths follow a general order: $V-O^t$ (t = terminal) < $V-O^b$ (b = bridging) < $V-O^p$ (p = phenolic) < $V-O^e$ (e = enolic). The V−O−V angles are very similar and are close to 113º, which is consistent with the reported values of analogous hydrazone complexes [5, 6, 7].

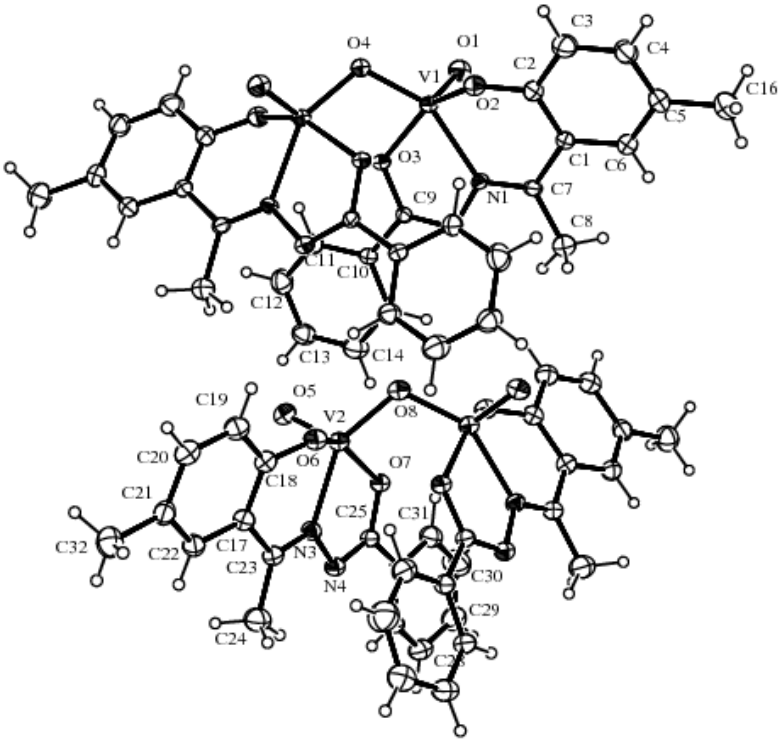


Fig. 2: Molecular structure of $[V_2O_3(L^2)_2]$ (with *C2/c* space group) with thermal ellipsoids drawn at 50% probability.

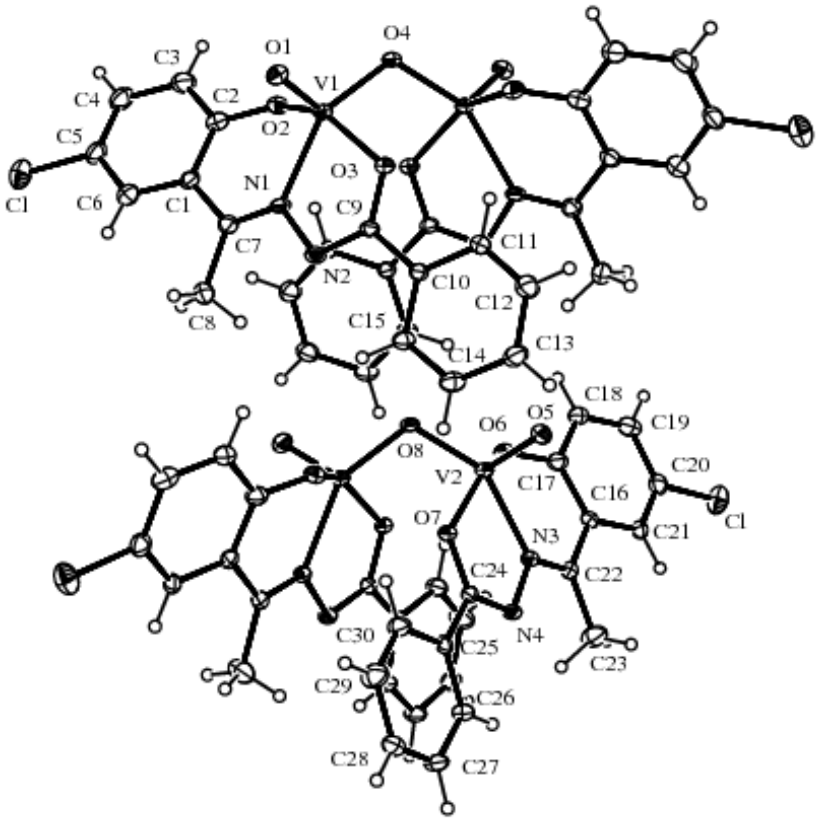


Fig. 3: Molecular structure of $[V_2O_3(L^4)_2]$ (with *C2/c* space group) with thermal ellipsoids drawn at 50% probability.

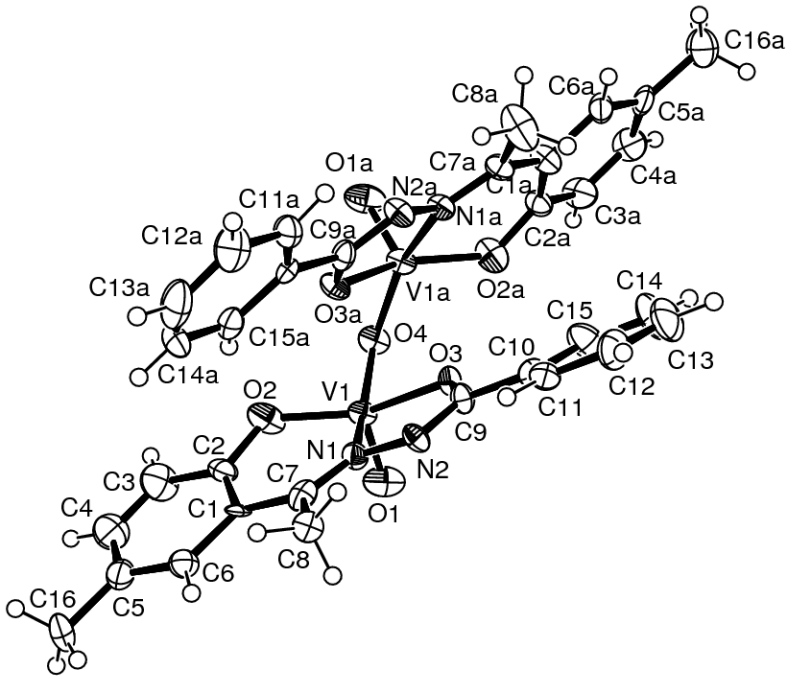


Fig. 4: Molecular structure of $[V_2O_3(L^2)_2]$ (with *Pbca* space group) with thermal ellipsoids drawn at 50% probability.

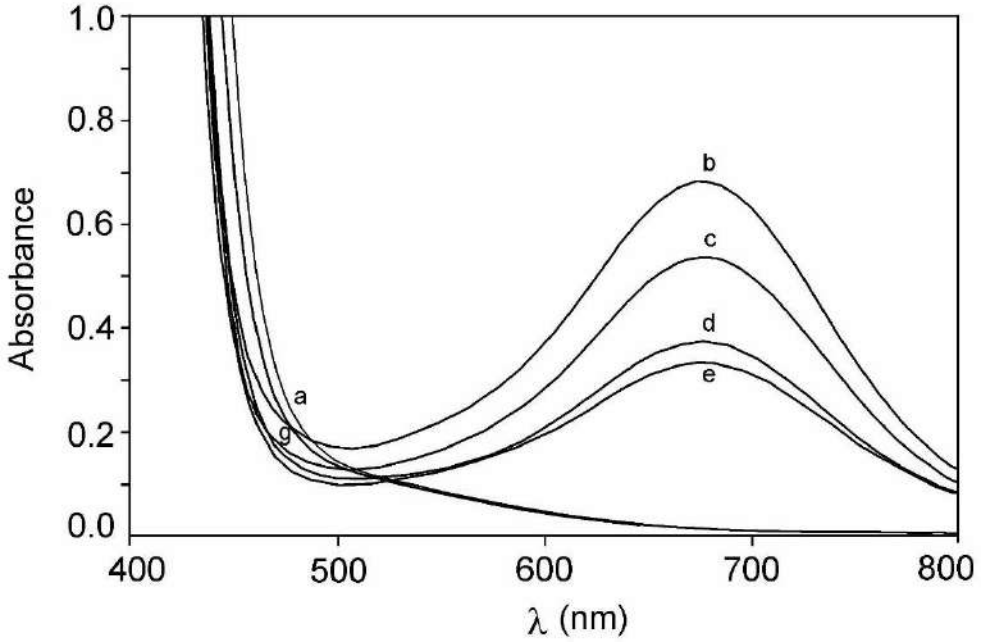


Fig. 5: Electronic spectra (400-800 nm) of a 7.973×10^{-4} mol dm^{-3} methanol solution of complex $K(H_2O)^+[VO_2L]^-$: (a) before the addition of ascorbic acid, (b) immediately after the addition of ascorbic acid, (c) 15 min after the addition of ascorbic acid, (d) 40 min after the addition of ascorbic acid, (e) 80 min after the addition of ascorbic acid and (f) 720 min after the addition of ascorbic acid. The concentration of ascorbic acid was about 10 times than that of the concentration of the complex.

Conversion of $[V_2O_3L_2]$ complexes to $K(H_2O)^+[V^VO_2L]^-$ and $[V^VOL(hq)]$ complexes

These dinuclear oxidovanadium(V) complexes can easily be converted to either mononuclear dioxidovanadium(V) complexes $K(H_2O)^+[V^VO_2L]^-$ or mixed-ligand complexes of the type $[V^VOL(hq)]$ on reaction, respectively, with two equivalents KOH in methanol and two equivalents 8-hydroxyquinoline (Hhq) in $CHCl_3$. The respective reactions are:

$$[V^V{}_2O_3L_2] + 2KOH + H_2O \rightarrow 2K(H_2O)^+[V^VO_2L]^-$$

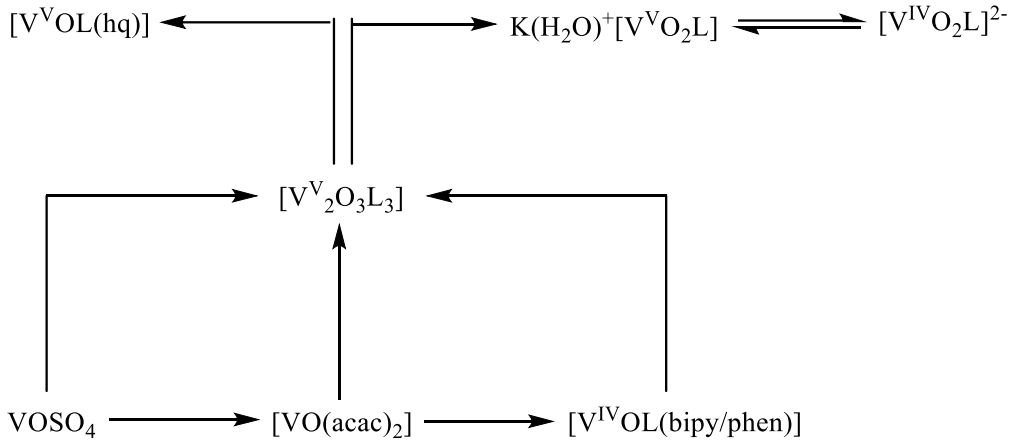
$$[V^V{}_2O_3L_2] + 2Hhq \rightarrow 2[V^VOL(hq)] + H_2O$$

Catalytic oxidation reaction of $K(H_2O)^+[V^VO_2L]^-$ complexes with ascorbic acid

The mononuclear dioxidovanadium(V) complexes oxidise ascorbic acid reversibly which was monitored spectrophotometrically. In each case after the addition of reducing agent a new band in the visible region near 675 nm was detected to a d-d transition of the resulting V(iv) species. After keeping the solution for sometime the intensity of the new band decreases gradually and finally the initial spectrum was obtained in a time interval ~ 12 hour. These observations strongly suggest that during the oxidation of ascorbic acid the dioxidovanadium(V) complexes are reduced by it to form the corresponding V(IV) complex presumably of the type $[VO_2(L)]^{2-}$ are not stable under this environment.

CONCLUSION

The four dinuclear trioxide Hydrazone complexes have been synthesized from various synthetic routes starting from different VO^{2+} precursors and these hydrazone ligands are very suitable for the stabilization of these motifs. The formation of these complexes from the decomposition of mixed ligand [VO(L)(bipy/phen)] complexes in CH_2Cl_2 solution indicates that these ligands have strong tendency for the stabilization of vanadium in its highest oxidation state(+V). These dinuclear complexes can be converted to the mononuclear binary complexes with VO_2^+ motif simply by increasing the (PH ~ 11) of the solution and mixed ligand ternary complexes with VO^{3+} motif by adding a monobasic bidentate strong chelating ligands. The dioxidovanadium(V) complexes can catalyze the reversible oxidation of ascorbic acid under aerobic condition which is biologically important particularly in relation to insulin enhancing activity.



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Synthesis,structure and solution chemistry of a family of dinuclear hydrazonato-vanadium(v) complexes with [OV(μ-o)VO]4+ core

Project Work

Submitted for partial fullfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. Bipul Mondal

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Reg. No.- A01-1112-112-015-2019

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Finally,my deepest admiration goes to my parents for their all-out support throughout my life

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Date:-14/12/2021

Place:-Rahara

Synthesis,structure and solution chemistry of a family of dinuclear hydrazonato-vanadium(v) complexes with [OV(μ-o)VO]4+ core

ABSTRACT:

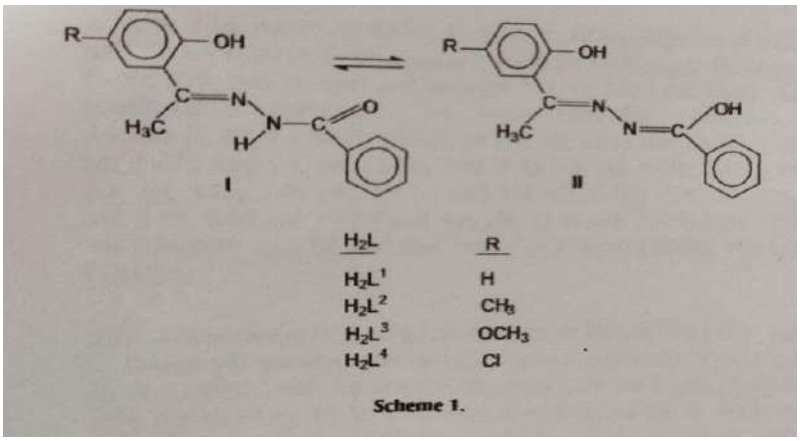
Dinuclear trioxidic [$(VOL)_2$μ-o](1-4) complexes were synthesized from the reaction of [$VO(acac)_2$] with an equimolar amount of H_2L [H_2L is the general abbreviation of hydrazone ligands H_2L(1-4)derived from the condensation of benzoyl hydrazine with either 2-hydroxyacetophenone or its para substituted derivatives] in acetone or dichloromethane or acetonitrile. Black monoclinic crystals of 2 and 4 with C2/c space groups were obtained from the reaction of [$VO(acac)_2$], respectively with H_2L(2 and 4) in acetone in which the respective ligands are bonded meridionally to vanadium in their fully deprotonated enol forms.

These dinuclear complexes are converted to the corresponding mononuclear cisdioxo complexes $K(H_2O)[VO_2(L)]$ (5-8) and mixed ligand [VO(L)(hq)] complexes on rection with 2 equivalent KOH in methanol and 2equivalents 8-hydroxyquinoline in chloroform. Ascorbic acid reduces the dioxovanadium(v) complexes reversively under aerobic condition

INTRODUCTION:

Vanadium is an interesting transition metal which has the ability to exist in a wide range of oxidation states starting from -III to +V. Vanadium easily switches between the oxidation states IV and V and the stabilization of either of these two states under aerobic condition depends upon the basicity of the coordinated ligand and also on the pH of the reaction medium. Of these three,the +V state has received considerable attention probably due to its two important properties: (i) it can exist in three motifs viz,mononuclear VO3+ and VO2+ motifs and dinuclear V2O34+ motif and (ii) it has the ability to exist in either 5 or 6 coordinated environment. These motifs are stable in soln around the physiological pH(~7) only when the metal is coordinated with sufficiently strong ligand for preventing the ppt. of hydroxides. This work was motivated by four objectives : (i) to synthesize the complexes containing V2O3(4+) core with a family of above mentioned hydrazone ligands , (ii) To rationalize the various synthetic routes for the formation of such type of complexes with this hydrazone ligands,(iii) To examine the feasibility of convertion of these dinuclear complexes into the mononuclear complexes with$VO(3+)$ and $VO_2(+)$ motifs and (iv) to study the effect of para substituents in the hydrazone ligands

on the electronic property of vanadium in these dinuclear complexes. With this background herein, we have used four tridentate dibasic hydrazone ligands [H_2L (1-4), general abbreviation H_2L the H's representing the dissociable phenolic and amide protons] derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone and its para-substituted derivatives.



Scheme 1.

Summary of the project work:

1. Materials - VOSO4.5H20, acetylacetone , Benzoyl hydrazine , 2-hydroxyacetophenone and its para-substituted derivatives were used as obtained. Hdrazone ligands H_2L (1-4) and [VO(acac)2] ligands were prepared following the methods reported in literature.

2. Synthesis of the complexes $[V_2O_3(L)_2]$ (1-4) – All the four dinuclear complexes (1-4) were synthesized by a simple general method using either $[VO(acac)_2]$ or $VOSO_4.5H_2O$ or [VO(L)(bipy/phen)] as the starting material.

Method – Orange red [VO(L1)(bipy)] (0.10 gm, 0.21 mmol) complex was dissolved in wet dichloromethane and kept at room temp. After 5 days black micro crystalline compound of 1 (0.061 gm , 88.40%) were obtained.The compound was characterized by elemental analysis and also by various spectroscopic methods. Complex 2,3,4 were synthesized in the similar fashion.

3. Conversion of $[V_2O_3(L)_2]$ complexes to $K(H_20)+[VO_2(L)]$- complexes –

(i) Conversion of $[V_2O_3(L1)_2]$ (1) to $K(H_2O)+[VO_2(L1)]$- (5) –

To a methanolic soln. of KOH (0.02 gm, ~0,3mmol) was added $[V_2O_3(L1)_2]$ (0.10 gm, 0.15mmol) and the rxn. Mixture was stirred for 4 hrs. at ~333K . An intense yellow soln. was obtained which was kept for slow evaporation at room temp. A yellow micro crystalline product of 5 obtained after 5 days , was filtered , washed with methanol and dried over silica gel. Yield 0.10 gm(83.03%)

2,3,4 complexes are converted to the 6,7,8 respectively in the similar fashion (analogous to 5)

4. Conversion of $[V_2O_3(L2)]$ complexes to [VO(L)(hq)] complexes –

(i) Conversion of $[V_2O_3(L1)_2]$ complex to [VO(L1)(hq)] complex

$CHCl_3$ solution 10 ml of 8-hydroxyquinoline (Hhq) (0.025 gm,0.17mmol) was added to a solution of $[V_2O_3(L1)_2]$(0.05gm,0.075mmol) in chloroform (20 ml).the yellow colour of the solution was changed gradually to violet. The mixture was stirred for 8h and the intense violet solution was filtered and the filtrate was left to evaporate slowly in the air .Shiny black crystalline product (0.065gm, 91.55%) obtained after 6 days was collected by filtration after washing with chloroform and then dried over silica gel,which was found to be identical in all respects with the compound [VO(L1)(hq)],which we have already prepared by different method. Other mixed-ligand complexes of this type with the H_2L(2-4) ligands were also obtained similarly by the reaction of Hhq with the respective $[V_2O_3(L)_2]$ complex.

5. Synthesis of dinuclear $[V_2O_3(L)_2]$ complexes and their conversion into their conversion into their mononuclear analogues-

$[V_20_3(L)_2]$ (1-4) complexes were prepared by various synthetic routes starting from VO2+ precursors –

$2VOSO_4 + 2H_2L + 4CH_3COONa + ½\ O_2 \rightarrow [VO(L)_2\mu\text{-}O] + 2Na_2SO_4 + 4CH_3COOH$

$2[VO(acac)_2]+2H_2L+1/2\ O_2 \rightarrow [VO(L)\mu\text{-}O] + 4Hacac$

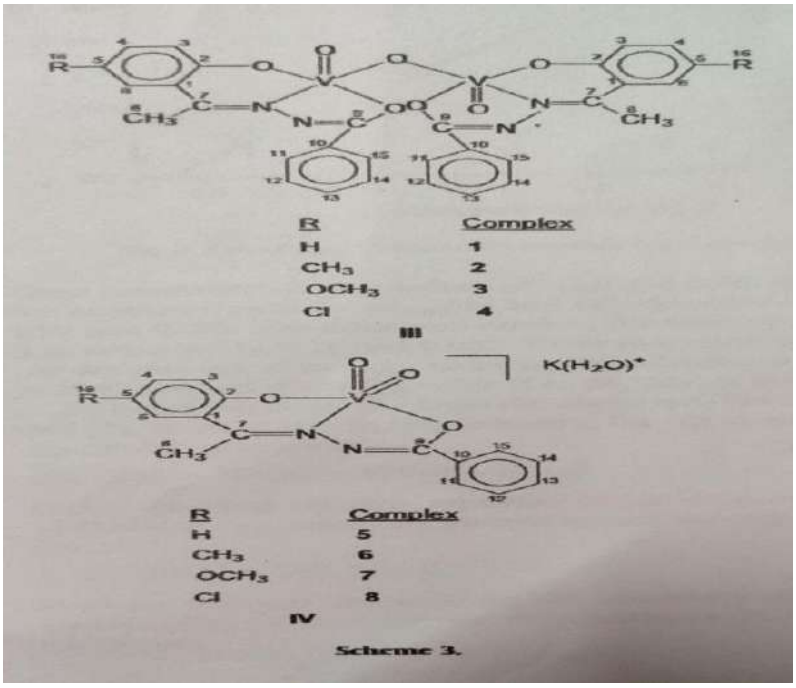
$2[VO(L)(bipy/phen) + ½\ O_2 \rightarrow [VO(L)_2\mu\text{-}O] + 2bipy/phen$

These dinuclear oxovanadium(v) complexes can easily be converted to either dioxovanadium (v) complexes (5-8) or mixed ligand complexes of type [VO(L)(hq)]-

$[VO(L)\mu\text{-}O] + 2KOH + 2H_2O \rightarrow 2K(H_2O)+[VO_2(L)]$-

$[VO(L)_2\mu\text{-}O] + 2Hhq \rightarrow 2[VO(L)(hq)] + H_2O$

Complexes(1-4) are freely soluble in chloroform but sparingly soluble in methanol. While complexes (5-8) are freely soluble in methanol,DMSO,DMF . But sparingly soluble in CH_3CN and insoluble in CH_2Cl_2.



Scheme 3.

6.Reaction of $K(H_2O)+[VO_2(L)]$-(5-8) complexes with ascorbic acid –

The reaction of $K(H_2O)+[VO_2(L)]$- complexes with ascorbic acid was monitored spectrophotometrically.In each case after the addition of reducing agent a new band in the visible region near 675 nm was detected to a d-d transition of the resulting V(iv) species .After keeping the solution for sometime,the intensity of the new band decreases gradually and finally the initial spectram was obtained in a time interval ~ 12 hour.these observations strongly suggest that during the reaction with ascorbic acid ,the $K(H_2O)+[VO_2(L)]$- complexes are reduced by it to form the corresponding V(iv) complex presumably of the type $[VO_2(L)]2-$.the reappearance of an almost identical original spectram (before reduction) after ~ 12 hour indicates that the ligand remained coordinated to the vanadium in the reduced V(iv) species and these reduced species are not stable under this environment.

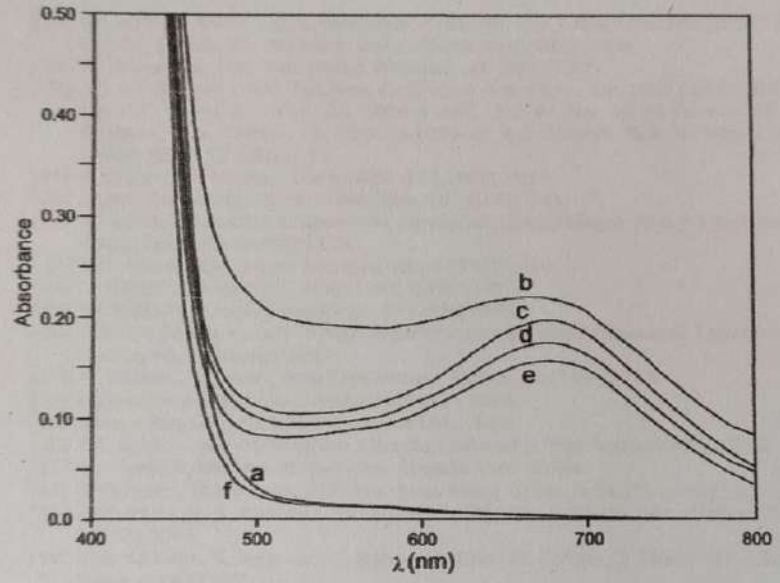


Fig. 7. Electronic spectra (400–800 nm) of a 7.973×10^{-4} mol dm^{-3} methanol solution of complex **2**: (a) before the addition of ascorbic acid, (b) immediately after the addition of ascorbic acid, (c) 10 min after the addition of ascorbic acid, (d) 30 min after the addition of ascorbic acid, (e) 60 min after the addition of ascorbic acid and (f) 720 min after the addition of ascorbic acid. The amount of ascorbic acid was about 10 times than that of the concentration of the complex.

CONCLUSION:

Hydrazone complexes (1-4) containing $V_2O_3(4+)$ motif can be synthesized following various synthetic routes starting from different VO(2+) precursors and these hydrazone ligands are very suitable for the stabilization of these motifs.The formation of these dinuclear complexes from the decomposition of mixed ligand[VO(L)(bipy/phen)] complexes in CH_2Cl_2 solution indicates that these ligands have strong tendency for the stabilization of V in its highest (+v) oxidation state. These dinuclear complexes can be converted to the complexes with VO_2+ motif simply by increasing the

(PH ~ 11) of the solution and to the complexes with VO(3+) motifs by adding a monobasic bidentate strong chelating ligand . The dioxovanadium (v) complexes are reduced reversibly by the ascorbic acid under aerobic condition which is biologically important particularly in relation to insulin enhancing activity.

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INHIBITION OF ZINC CONTAINING METALLOENZYME: A WAY TOWARDS CANCER TREATMENT

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. Ranjan Patra

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Registration No.: A01-1112-112-006-2019

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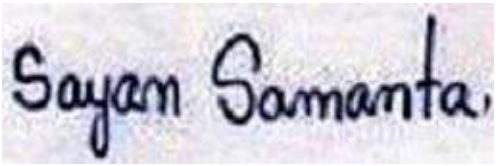

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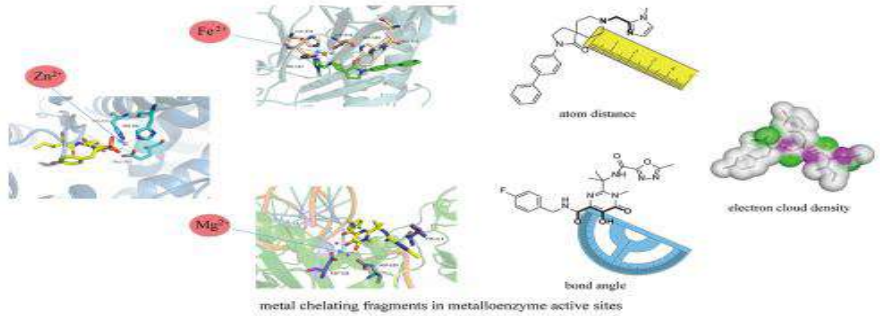
Date: 15/01/2022

Place: Rahara

INHIBITION OF ZINC CONTAINING METALLOENZYME: A WAY TOWARDS CANCER TREATMENT

ABSTRACT:

For platinum based anticancer agent DNA is considered to be the primary target and also gained great success in clinics but a serious side effects are observed for DNA targeted anticancer drugs. As a result, search for novel therapeutic drugs is stimulated and it is observed that Zn containing metalloenzyme can be used as an alternative for metal based anticancer agents. Metal dependent enzymes (i.e., metalloenzymes) are part of all enzymes and crucially important in a wide range of biological process such as DNA modification, protein homeostasis, antibiotic resistance and many others. Consequently, metalloenzymes represented a vast and largely unexplained space in the field of drug development. Inhibitors of metalloenzymes are mainly mimics of substrates of the corresponding enzyme for the enzyme. The peculiar features of coordinate complexes have aided in this review, such as i) Simplified 3D structures which increase enzyme binding selectivity and affinity. ii) Designing of enzyme inhibitors with multiple modes of action due to redox activity of metal complexes. Now the discovery of therapeutics that target metalloenzymes are a part of both bioinorganic and medicinal chemistry. Fragment based drug discovery (FBDD) is very important drug discovery approach and also well needed for the development of metalloenzyme inhibitor. For metalloenzyme inhibition, a metal dependent active sits are highly required. Till now, Survey of many molecular fragments for binding the metal active sites of metalloenzymes is still undiscovered. Several questions are raised on the application of FBDD for the development of metalloenzymes such as how the particular fragments for a given metalloenzyme can be found. Among all the questions, most significant and concerning are based on specificity i.e., whether a particular metalloenzyme can be specific and selective as other small molecule inhibitors (inhibitors do not have metal ion at its active site). The review article mainly focused on zinc containing metalloenzyme inhibition of metal based anticancer agent, different metal binding fragments and their chelating properties and through FBDD an effort is also performed to connect between bioinorganic & medicinal chemistry.



metal chelating fragments in metalloenzyme active sites

INTRODUCTION:

It is universally known that metal ions, especially bivalent metal ions are essential to living organisms. Within all enzymes metalloenzyme consists more than 30% of it. Metalloenzymes are very important to nearly all biological process and hence it is used for drug development for a wide range of disease. Chelating properly of fragment with metal is now an effective strategy in the medicinal chemistry and most common examples of it is cancer.[1] Though platinum-based anticancer drugs are discovered as an effective anticancer agent but it has serious side effects and acquired drug resistance in cancer chemotherapy.[2] Since DNA is their primary target, it can damage normal cell during DNA binding mechanism and cause serious side effects.[3-4] From recent research in the field of genomic and proteomics it is said that various enzymes related to the progression of cancer has discovered. Therefore, for cancer treatment research of anticancer agent that target enzymes has become the preferred approach.[5-8] For the inhibition of targets, these drugs mostly use co-ordinate covalent bonding towards the active site of metal ion. In spite of many anti cancer strategies, chemotherapeutic resistance is still a major challenge in current clinical practice. **Statistical analysis has shown that among 1371 enzymes with known 3D structures registered in Protein Databank SwissProt Enzyme Classification (PDBSProtEC) database[9], 558 of them are annotated as metal-dependent**.[10] "A recent review indicates that less than 70 FDA approved drugs are metalloenzyme inhibitors, targeting only 7 classes of metalloenzymes"[11]. In between 1500 FDA approved drugs; the above data suggested that less than 5% of small molecule drugs that target metalloenzyme. Hence a large deviation between the no. of potential metalloenzyme targets and the number of drugs developed for these targets manifests backwardness in developing metalloenzyme inhibitors. Metalloenzymes have Zn (II) as a vital component of the holoenzyme which contributes to its catalytic and structural functions.[12] A major limitation in this field of metalloenzyme inhibitors is limited number of HBPS can be successfully bind to the active site of metal ion. Now this limited explanation of HBPS can be illustrated by considerable efforts to make inhibitors of matrix metalloproteinases (MMP), a type of Zn dependent metalloenzyme call for a wide range of biological process. For nearly 20 years, these MMPs were a prominent metalloenzyme target for the development of cancer therapeutics. For the inhibition of Zn dependent MMP, hydroxamic acid functional group can be used which is mainly found in siderophore like natural products.[13] It is also used in many drug discovery efforts to identify other metalloenzyme inhibitors.

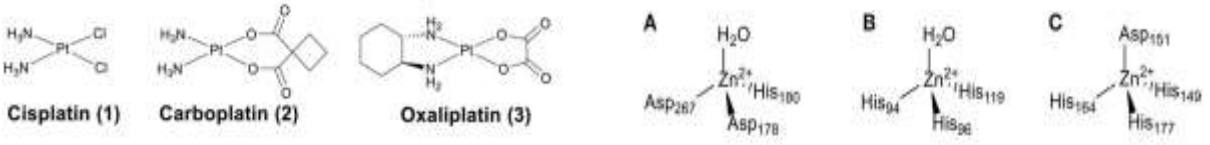
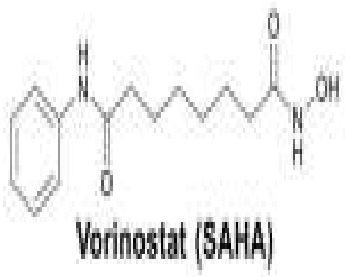


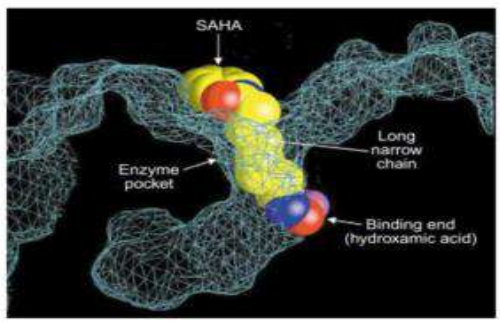
Figure-1: Chemical structures of platinum drugs approved by the FDA (1–3). The Zn (II) ion coordination in the (A) HDAC8 (Finnin et al., 1999), (B) CA II (Eriksson et al., 1988), and (C) MMP2 (Morgunova et al., 2002) active site.

RESULTS & DISCUSSION:

Zn (II) dependent enzyme and their inhibitors:

Metalloenzymes have Zn (II) ion as a vital component of the holoenzyme, which contributes to its catalytic and structural functions. It is seen in studies that the Zinc containing metalloenzymes are invested in the pathogens of irregularities as simple as infections to the complex disease cancer. Zinc containing metalloenzymes like HDACs, CAs and MMPs are shown to be present over threshold value in cancer patients. HDACs show prevalence in lungs, colon, breast and prostate cancer.[14] Likewise CAs is overexpressed in lung, colon and GI stromal cancers.[15] MMP expression is exaggerated in cervical cancer[16] and primary nodular melanoma.[17] Predominantly these three metalloenzymes containing Zn (II) ion as their metallic component, all seen to be involved in the pathophysiology of tumorigenesis.[18-19] Researches have aimed these metalloenzymes as an alternate target for anticancer drugs.[20-21] The therapeutic mode of action targeted is the modulation of the enzymatic activity of Zinc containing metalloenzymes. Enzyme inhibition is already practiced with the help of metal complexes. The peculiar features of co-ordinate complexes have aided in this view, such as, i) the hydrophobic spaces of the enzyme lattice can perfectly fit the 3D coordinate structure.[22-23] ii) When subjected to hydrolysis, amino acid side chains of the enzyme bind to the unstable metal-ligand bond of the complex. iii) Apart from these, the photophysical and photochemical properties redox activities of the metal complexes make it a very suitable to design enzyme inhibitors with anti tumor mechanisms of various modes.[24] Thus the anti tumor potential of co-ordinate metal complexes provide a definite edge on the production of anti-cancer drugs, mainly targeting the Zinc-containing metalloenzymes. SAHA is the first FDA approved HDACi to enter the clinic and crystal structure of human HDAC8 complexes with SAHA is shown in figure below.

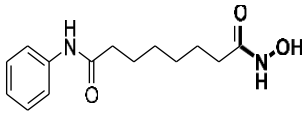




1. Histone deacetylase

The deacetylation of lysine residues on histone is catalyzed by HDACs, thus regulating the entry to DNA by changing the chromatin structure.[25] Till now, a total of 18 HDACs have been found. They are divided into 4 categories. Class I consists of HDAC1, 2 and 8; chain IIA

consists of HDAC4, 5, 7 and 9; chain IIB contains HDAC6 and 10; class III is called as surtuins1-7, while class IV consists of only 1 member, HDAC II. Except member of class III, all of the histone deacetylases are metal dependent.[26] HDACs are seen as therapeutics targets for variety of diseases such as cancer, fibrosis, autoimmune disease, inflammation and metabolic disorders.[27] Recent researches discovered a series of new biological activities including antifungal,[28] anti-aging,[29] antidepressants[30] and neuroprotection.[31] Additionally, HDACs also remove other acyl modification from the lysine groups like propionylation, crotonylation and myristoylation,[32] especially HDAC11.[33] HDACs are generally classified into hydroxamic and non-hydroxamic. Some hydroxamate derivatives retain the typical fragment of suberoylanilide hydroxamic acid (SAHA, Vorinostat, compound: 1), the first clinically approved HDAC inhibitor (HDAC I) used for treating cutaneous T-cell lymphoma.[34] Compounds 2, 3 and 4 adopt the six-carbon aliphatic chain of SAHA. Compounds 2 and 3 are both Class I HDAC inhibitors. Potent cytotoxic activity is displayed by Compound 2 against colorectal adenocarcinoma HT-29, neuroblastoma SH-SYFY and breast adenocarcinoma MCF-7, while toxicity towards ovarian cancer A2780 cell is shown by compound 4.[35-37] In 2015, a series of phenylglycine-based HDAC inhibitors with Y shaped caps (compound: 5) were reported by zhang and his colleagues. They also discovered the correlation of topological polar surface area (tPSA) value, cell permeability, and antiproliferative potency.[38] In 2017, Yong and his co-workers replaced the secondary amine with a tricyclic beta-carboline moiety (e.g.: 6) while indole alkaloids pass intrinsic antineoplastic activities.[39] In 2018 a series of Y shaped fan HDACIs were disclosed by Yu et.al. (e.g.-7) which is actually a ring opened analogue of [40] 6. Non-hydroxamic inhibitors like compound-8 chelate the Zinc ion via its 2-amino benzamides moiety.[41] Parasitic infection like Schistosomiasis is similar to cancer in some aspects was revealed by recent studies. For example, parasites, like tumors exhibit high metabolic activities, uncontrolled cell division, lactic acid is used as source of energy posses the ability to escape from immune surveillance. Thus, during the development of antiparasitic drugs, drug targets related to anticancer treatment are studied. Transcriptomics studies revealed that Schistosoma HDACs (smHDAC8) is predominantly expressed during the life cycle of Schistosoma. In comparison to the human HDACs (hHDAC), smHDAC is not conservative; six large insertions have been found in the protein sequence. Thus HDAC 8 is supposed to be a promising drug target.[42]



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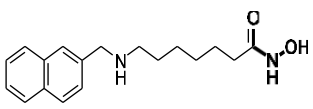

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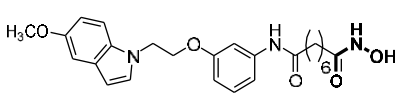

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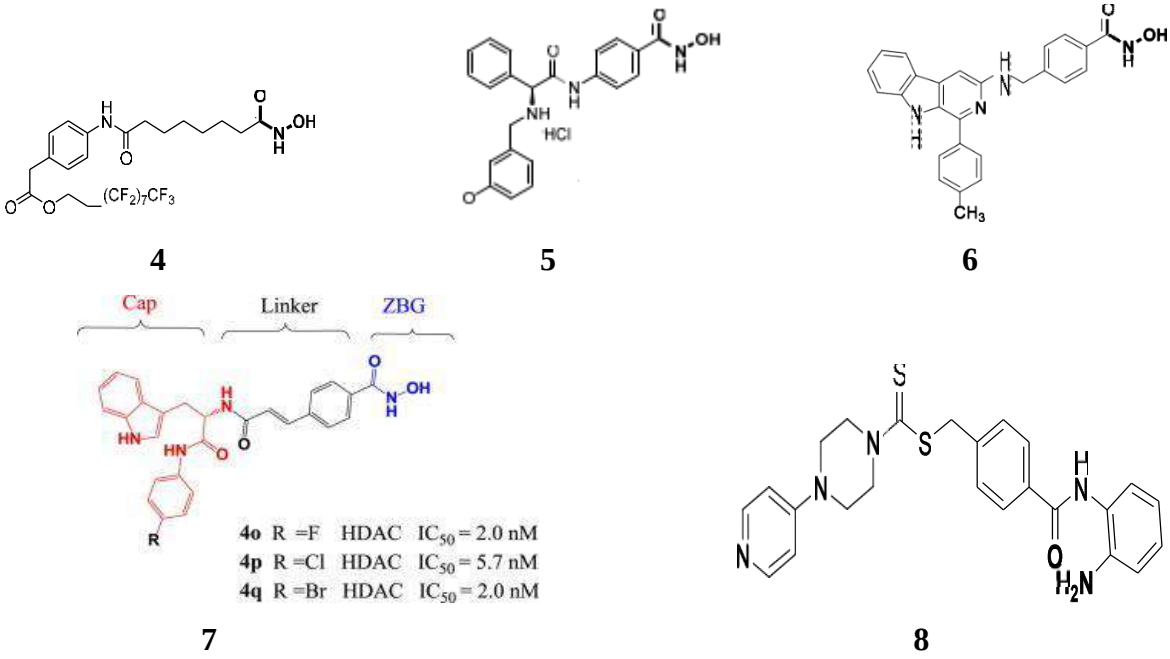


4 **5** **6**

7 **8**

Figure-2: HDAC inhibitors containing Zn^{2+} chelating group

2. Matrix metalloproteinase

Matrix metalloproteinases are a class of Zn^{2+} dependent endopeptases which are indulged in the degradation of extra cellular matrix and cell membrane components such as proteoglycan, collagen, elastin, fibronectin, gelatin, laminin etc under normal physiological conditions, MMPs are indulged in the maintenance of extra cellular matrix homeostasis, tissue remodeling, wound healing, angiogenesis, apoptosis, and other important physiological processes.[43] However MMPs also induce the initiation and progress of a number of harmful diseases like cancer,[44] neurodegenerative disease,[45] kidney disease,[46] diabetic neuropathic pain[47] and HIV-related diseases.[48] There are more 20 kinds of MMPs and they are divided in various ways according to the point of view considered. For example, according to their distribution in the cell, they can be divided into two groups: secretary and membrane binding enzymes. According to the substrate specificities and amino acid sequences, they are mainly divided into 5 categories: collagenases, gelatinase, stromelysins and matrilysins. Among all the MMPs, cytoplasmic related MMPs are inhibited by alpha-macro globulin secreted by the liver, while extracellular MMPs are regulated by endogenous tissue inhibitor of metalloproteinases.[49] A large number of MMP inhibitors have been developed but clinical trials were not particularly successful. This was as some of the earlier discovered drugs, such as marimastat (compound-1, Fig: 3) were broad-spectrum MMP inhibitors.[50] Hence, a series of MMP-1 sparing inhibitors were created and tested, where compound 2 partially inhibited MMP-13 with an IC_{50} value of 0.42 nm.[51] Later on, more hydroxamate based selective inhibitors were searched. For e.g., compound 3 was a subnanomolar inhibitor of MMP-2 and MMP-9;[52] whereas compound 4 was found to show excellent MMP inhibitory action in the range of nanomolar (MMP-2, -8, -9) and

picomolar (MMP-13). To generate a good tool for noninvasive positron emission tomography (PET) imaging compound 4 was further radiolabel with [18F]. It is noted that, compound 4 showed no off-target effects toward the other tested metzincins (such as ADAMs and meprins).[53] Scientists have also tried to develop inhibitors with new ZBGs. After indolactam scaffolds (5, Fig: 3) having different Zinc binding groups were reported,[54] structures having pyrone[55] (compound 6), pyridinone[56] (compound 7) and 6-,7- or 8-membered ring derivatives of pyridinone[57] (such as compound 8) were successively disclosed, where a potential inhibition towards MMP-2 and MMP-3 is shown by compound 6. Also, Nara and team developed a novel clan of MMP-13 inhibitors that contains a 1,2,4-triazol-3-yl group as a ZBG. The most promising compound 9 showed excellent potency (IC_{50}=36pm) and selectively (greater than 1500-fold) over other MMPs. From x-ray analysis, it is confirmed that the 1,2,4-triazol-3-yl moiety coordinated with the catalytic Zn^{2++} center in monodentate manner.[58] Recently, Nguyen and team discovered a new selective MMP-2/9/14 inhibitor (compound 10), used as a candidate drug for treating diabetic foot ulcers. [59]

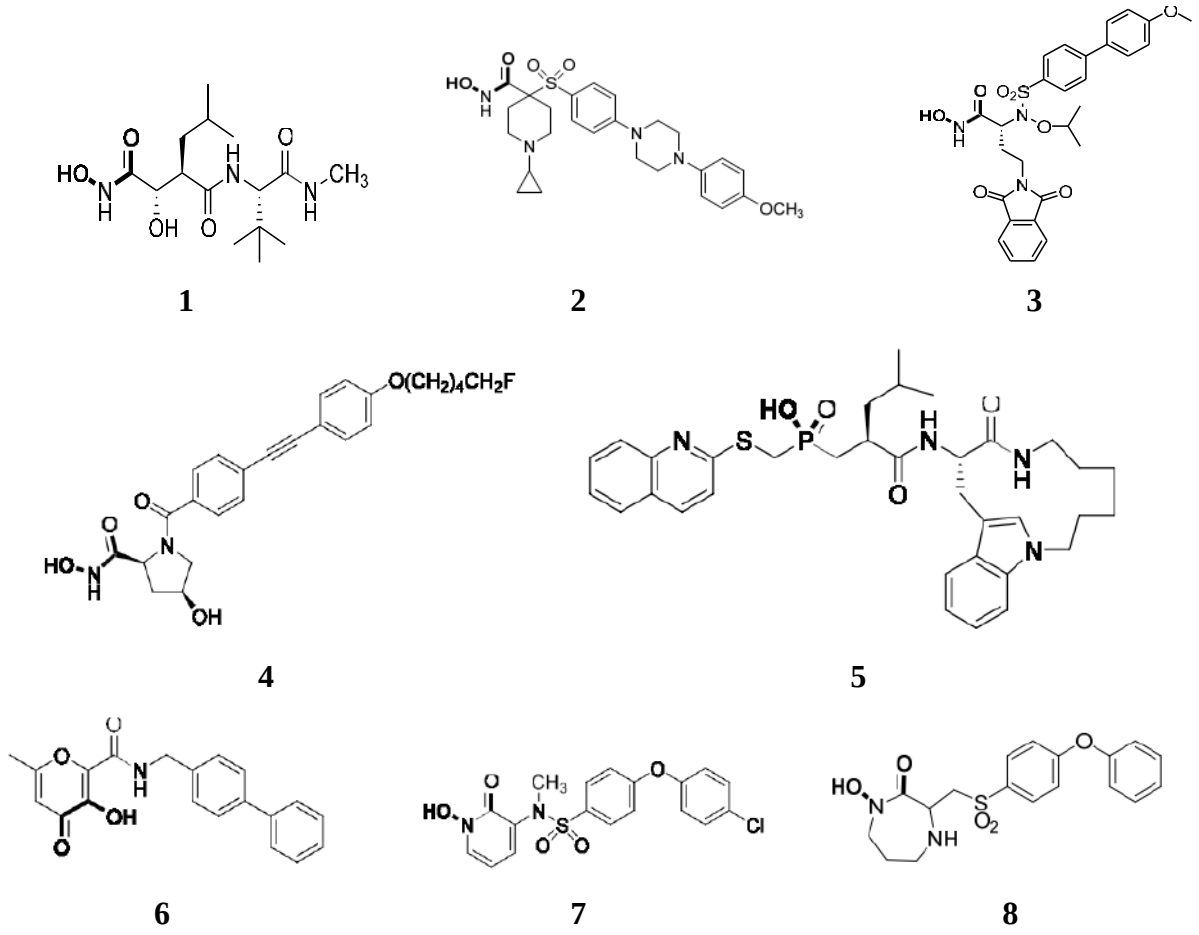
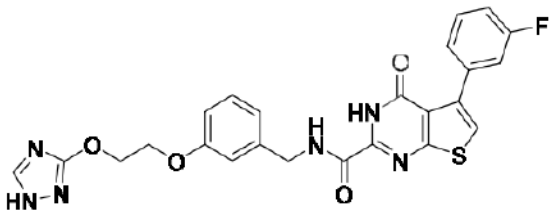


Figure-3: Matrix metalloproteinase inhibitors containing Zn^{2+} chelating group.



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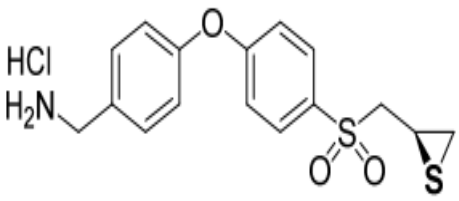

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3. Carbonic Anhydrase

Among the Zn2+ containing metalloenzymes, CAs was the first enzyme to be discovered. Although in some species like plants, archaea, fungi CAs contain other metals like Fe2+, Co2+ etc. CA catalyzes reversible hydration of CO2 to for bicarbonate. The reaction involves 2 steps- a nucleophile attack on CO2 followed by regeneration of Zinc hydroxide. CAIs are used in treatment of glaucoma and cancers. The modus operandi of CAIs in Glaucoma treatment is to primarily reduce aqueous humor formation. Production of bicarbonate is reduced which lowers the osmotic gradient b/w AH and plasma thus reducing water flow into aqueous/anterior chamber. In addition to that CAs has a pertinent role in acid base equilibrium regulation in tumor cells. Tumorigenesis involves excessive proliferation which creates a hypoxic and acidic environment in extracellular matrix. CAs helps the tumor cell growth by stabilizing intracellular pH to match physiological values. Other than this other diseases related to CA are neurodegenerative disorders,[60] ischemia-reperfusion induced acute lung injury[61] and parasite-associated diseases.[62-64] CAs can be genetically divided into seven groups.[65] Alpha-CAs are predominantly found in vertebrates and the only type found in mammals.[66] Alpha-CAs also has 15 isotopes, out of which 12 have a coordination centre with Zinc in their active sites (CAs-I-IV, CAs-Va-Vb, Ca-VI-VII, CA IX and CA XII-XIV).[67] Among the CAIs explored, sulfonamide-containing majorities are in abundance.[68] Supuran in 2002 reported series of aromatic and heterocyclic sulfonamides having anti epileptic properties and from maximum electroshock seizures test it is observed that compound 1 (Fig: 4) was the best inhibitor.[69] In 2006, Christianson noted various unique "two-prong" inhibitors having benzenesulfonamide and cupric iminodiacetate moieties. From compound 2, it is explained that Zn (II) participate in chelating with NH group of sulphonamides and the iminodiacetate part binds to H64 of CA and H200 of CA (Fig: 4, 14).[70] Dudutiene in 2014 found many CIAs with large steric hindrance groups. Crystal structure of CAs with compound 3 showed cyclooctyl groups fits only in this hydrophobic pocket in active site of CA, proving its selectivity.[71] In further times, plasmon resonance and fluroscent based thermal shift assays showed many CA-ligand pairs.[72] Recently Salerno and his colleagues showed many novel benzenesulfonamide compounds containing bi/tricyclic scaffolds. Compound 4, selectively inhibited tumor associated hCA-IX, Ki belong

0.79 nm, more potent by 32.7 times more than positive control acetazolamide.[73] Many moieties have been incorporated into classical Zinc binding benzenesulfonamide groups to enhance selectivity, affinity and membrane permeability of molecules, including glucosamine derivatives (compound-5) [74], curcumin scaffold (compound-13) [75], isatin scaffold (compound-6) [76], 1,3-diaryltriazene linker (compound-7) [77], ureido linker (compound-8)[77], amino acid moieties (compound-9)[78] and NO-releasing moieties (compound-10). [79] Annuziato discovered series of N-oxide pyridine derivatives (compound-11) showing antifungal activities. Studies showed N-oxide group chelating the Zinc.[80] Nocentini reported other groups of antifungal inhibitors containing monothiocarbonate scaffolds (compound-12). Quantum mechanics calculation showed sulphur atom bound to Zn^{2+} in a tetrahedral structure. Other non-classical moieties studied are phenols, polyamines and carboxylic acids. Sulfonamide appears to be the best ZBG for formation of potent inhibitor of all CA isoforms, but other ZBGs candidate to generation of selective CAIs providing data for chelating studies.

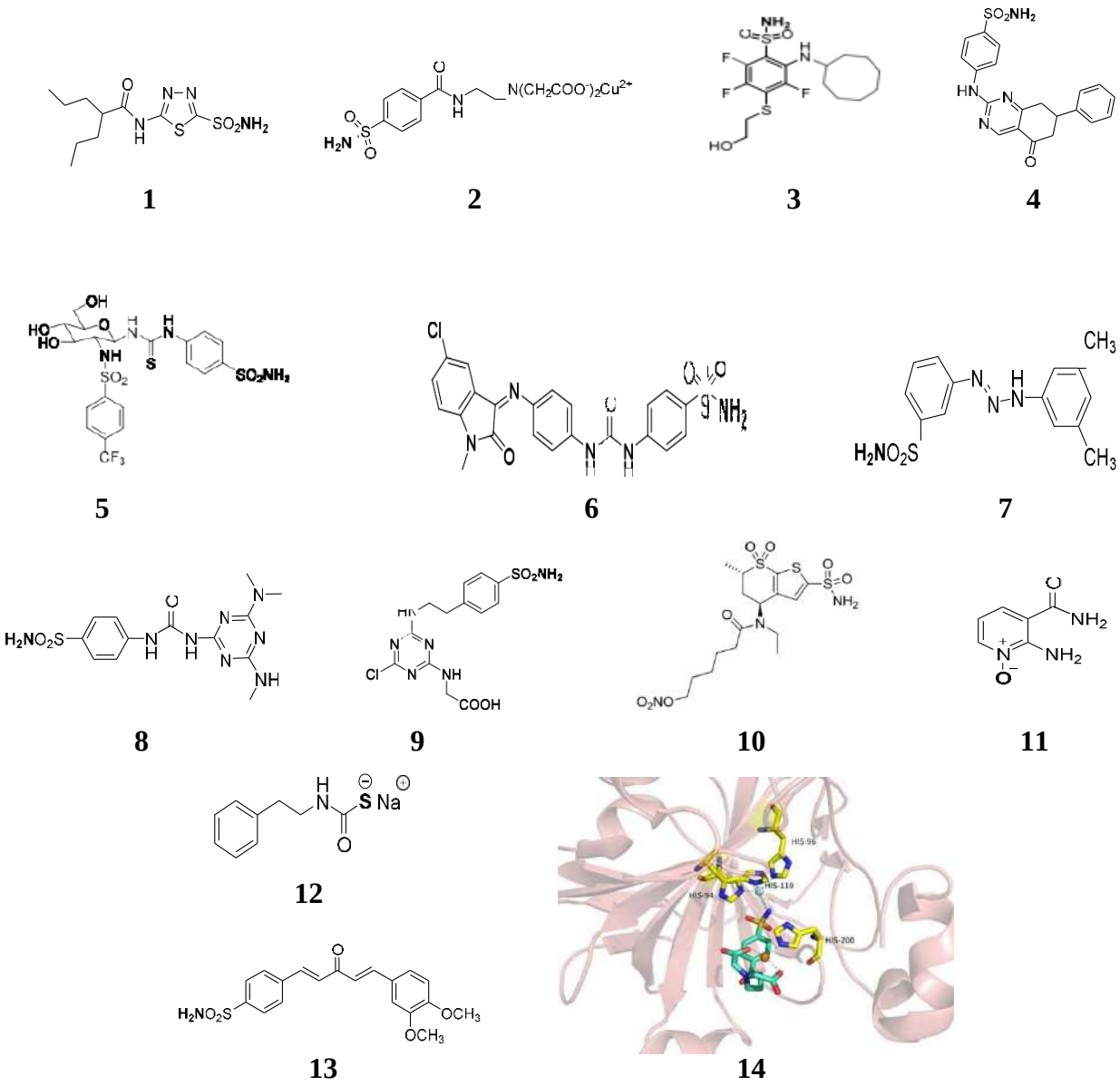

Figure-4: Carbonic anhydrase inhibitors containing Zn^{2+} chelating group

Expose of the hydroxamic acid myth:

To introduce feasible alternatives to the hydroxamic acid MBP (metal-binding pharmacophores), it is necessary to satisfy those interested in metalloenzyme inhibitor that the hydroxamic acid could be distinguished and did not create a silver bullet. For doing this it was necessary to take an existing metalloenzyme inhibitor and notice that substitution of a hydroxamic acid with an alternative MBP can lead to an inhibitor with more improved activity. This was a first step to initiate such protocol and also able to attract the attention of medical chemistry community. As MMP inhibitors do a considerable amount of work and they depend upon the hydroxamic MBP[81], MMPs were selected for their initial investigation. Main target was to take a known MMP-3 (stromelysin) inhibitor reported by Fesik[82] [compound SF-3, Fig: 5] and carry out a single atom substitution, which shall transform the hydroxamic acid MBP into a thiohydroxamic acid

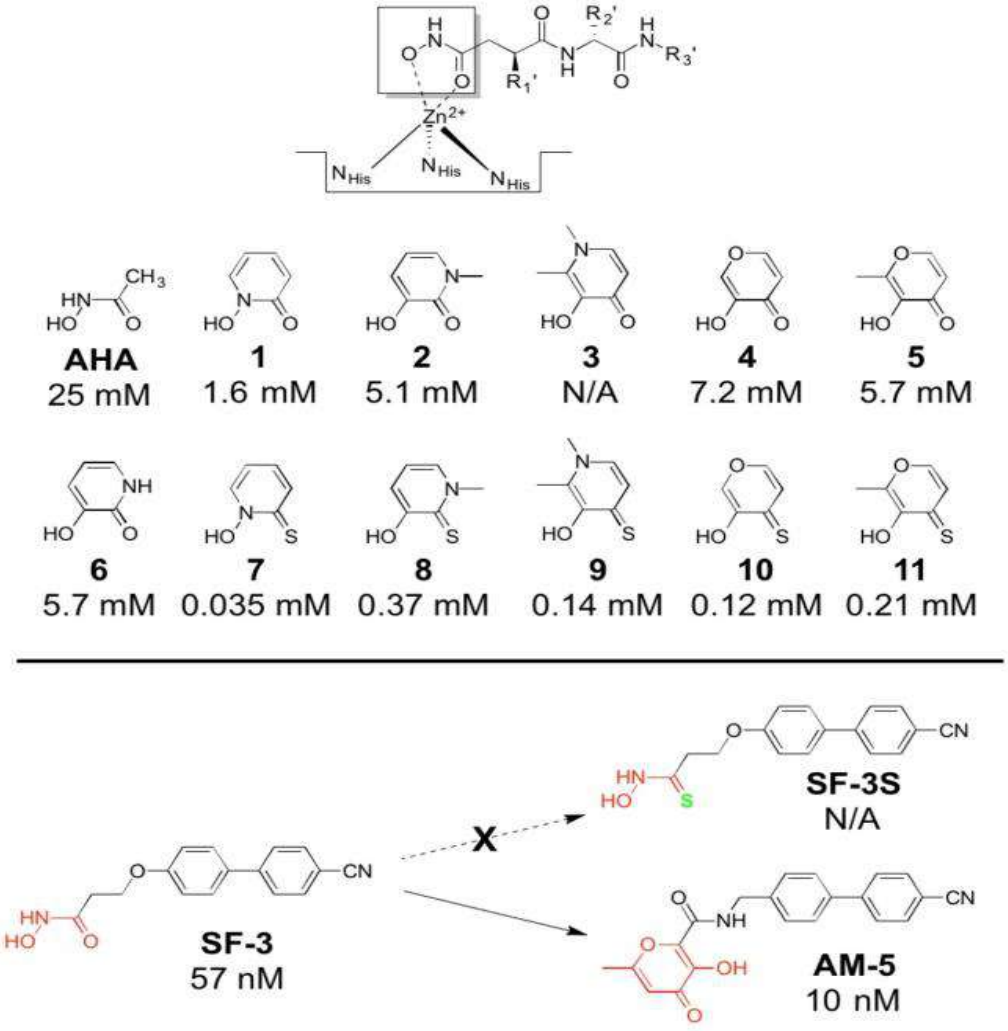

Figure-5: (top) Scheme of a generic hydroxamic acid inhibitor binding to an MMP active site. Alternative MBPs (1−11) were all found to be more active than a hydroxamic acid MBP (acetohydroxamic acid, AHA). (Bottom) To demonstrate the utility of alternative MBPs, a known MMP-3 inhibitor (SF-3) was modified (MBPs highlighted in red). Attempts to make a thiohydroxamic acid analog (SF-3S) were unsuccessful, but use of a maltol-based MBP (AM-5) led to a substantial improvement in activity. IC50 values shown below each compound are against MMP-3.

MBP (compound SF-3S, Figure 5) with the help of intermediate hard soft acidity of the Zn (II) ion at the MMP active site. Such an important upgradation in inhibitor binding by simple switch MBP donor atom from oxygen to sulphur would explain that there were possible alternative to the hydroxamic acid MBP. There are so many limitations in this technique such as synthetic challenges, poor solubility and questionable chemical stability of the thiohydroxamic acid. Still there is a tendency to traverse related derivatives, which could behave as alternative MBP fragments [Figure-3, 1-11]. These other MBPs were expected to be more active that acetohydroxamic acid on the basis of several features, such as conformation acidity, graded rigidity, and preferred hard-soft donor atom set. Now, routine enzymatic were done against MMP-3 by these MBPs.[83] This illustrates the advantages of MBP fragments in comparison to conventional fragments, where the tighter binding of metalloenzyme allows for.[84-85]

Determining metalloenzyme inhibitor selectivity:

Though several metalloenzyme inhibitors approved the clinical trial, some biasness is still arrived against the development of this therapeutics. This biasness is developed from a thought that any compound bearing this MBP will be non-selective in nature and as a result they will either off the mark from metalloenzyme inhibition, disturbing the normal metal ion homeostasis or both. Hence this FBDD approach for developing improved metalloenzyme inhibitor is reviewed whether they exhibit as a broad class of medicinal property, since it can co-ordinate on the active site of metal ion with their own molecular mechanism of action. To

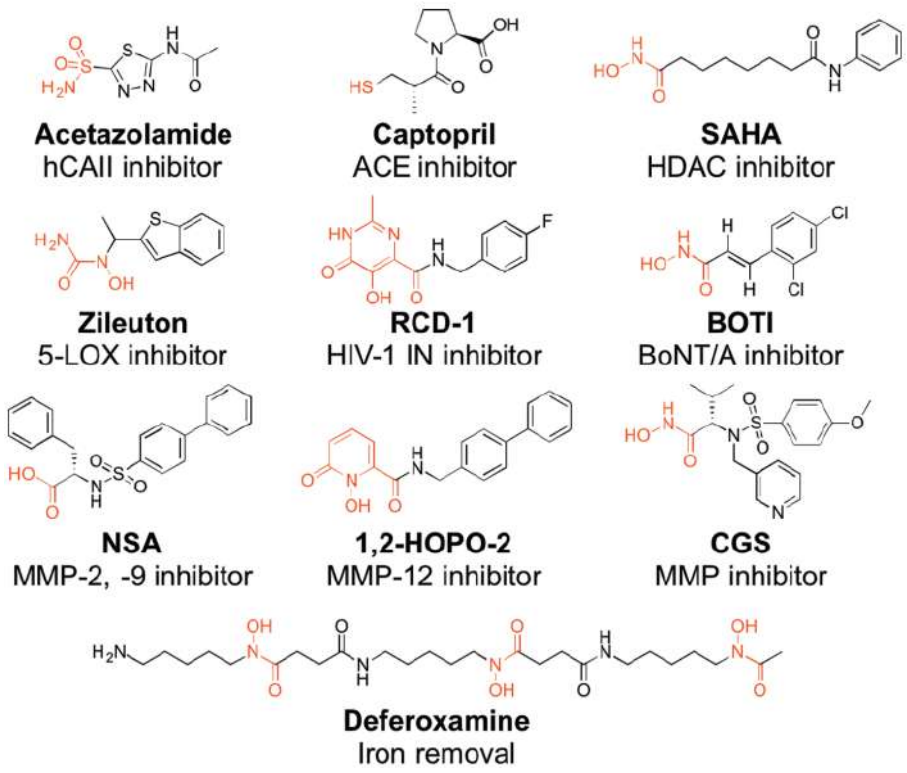

Figure-6: Metalloenzyme inhibitors and their targets examined for inhibitor selectivity. MBPs are highlighted in red.

test the poor selectivity of metalloenzyme inhibitors, a panel of metalloenzyme and their inhibitors were examined in cross-inhibition assays.[85] A list of tested metalloenzyme inhibitor as well as their respective targets is shown (figure: 6). The inhibitors scrutinized include a large no. of chemical structures and MBP motifs, covering sulphonamides (acetazolamide), thiols (captopril), hydroxamic acids (SAHA, CGS) and others. The prior mentioned experiments were centered on evaluating the selectivity of metalloenzyme inhibitors for off target inhibition. A separate but related concern centre throughout the possibility of metalloenzyme inhibitors interfering with metal ion homeostasis, trafficking and metabolism. Two sets of experiments were carried out to evaluate this topic. Firstly, the iron removing ability of metalloenzyme inhibitors from transferrin and secondly the effect of sublethal concentration of histone deacetylase, (HDAC) inhibitors on the metal ion distribution and content of mammalian cells. In the first set of experiments, to remove iron from holotransferrin was evaluated and the ability of the inhibitors were listed (in Fig: 6). None of the components have shown any iron removal even at concentrations of 1mM, except for 1, 2-HOPO-2 (fig: 6) that showed a few activities which are below that of the bacterial siderophore desferroxamine (an FDA-approved iron chelator).[85] As among the most accessible transition metal pools in human, transferrin is represented and as such is the target of bacterial siderophores (e.g., desferroxamine, fig: 6). By this data it is suggested that metalloprotein inhibitors are incapable of disrupting metal ion homeostasis, at least via this trafficking pathway.

Figure-7: HDAC inhibitors with different metal-binding ability (MBPs highlighted in red). IC50 values are listed for the HDAC isoform for which each inhibitor is most active.

In the second set of experiments, three separate HDAC inhibitors were examined for their propensity to alter the metal ion content distribution in the mouse fibroblast NIH3T3 cell line.[86] As those three HDAC share a common metalloenzyme target (i.e., zinc dependent HDACs) therefore was selected for the experiment but those possess different MBPs with vastly different metal-binding affinities. Hence, the aim was to distinguish between changes in metal ion metabolism as a function of HDAC inhibitors (which all inhibitors should display) versus that caused by a greater affinity of one of the inhibitors to bind metal ions. Because of the difficulty in these experiments some combinations of methods were utilized that includes inductively

coupled plasma atomic emission spectroscopy (ICP-OES), energy- dispersive x-ray fluorescence microscopy (SXRF). To monitor whole cell metal content ICP-OES was used, while EDX was used to examine overall context and changes in the distribution of one metal ion (Zn). Eventually within the limits of these techniques, no prominent changes in metal ion content or distribution were observed upon the treatment with sublethal concentration of HDAC inhibitors.[86] These results with other findings that are described earlier collectively guide us to the same conclusion that came up in 2013[85] that is for off-target activities metalloenzyme inhibitors do not possess any greater risk than any other class of small molecule enzyme inhibitors.

CONCLUSIONS:

Now days, the application of metal-ligand in the field of medicinal chemistry for treating cancer patient is well established. In this review, we have explained metal-based compounds with Zinc containing metalloenzyme and their inhibiting approach towards cancer treatment. From above examples, we can say that in comparison to metal moiety or organic inhibitor alone, these metalloenzymes are more powerful in their biological activity and it recommends that the conjugation of known organic inhibitor with a metal center can outcome in a co-ordinate advantage. Particularly, these Zn containing metalloenzymes are more effective than platinum-based drug in cancer treatment in the field of sensitivity and resistant cell lines, which explains its fruitfulness to overcome the limitations of Platinum based chemotherapy. Taking into consideration, the clinical success of some metal based anticancer agent and the potential and potential of metalloenzyme as drug target, we may expect that flourishing years are coming. From literature survey, it is reported that most of the metalloenzyme inhibitors inhibit all enzyme isoforms non-specifically, so called pan inhibitors. It has been noted that due to toxicity in the clinic, their potential in the field of solid tumor is limited (Bieliauskas and Pflum, 2008). Since most of the enzyme contains two or more isoforms with their unique gene expression and differ in cellular positioning and function limitation in the pan-inhibitors are arrived. By destroying multiple cellular internal processes related to growth and metastasis of the tumor, it also affects the normal physiological function. As a result, potentially toxic side effects of pan-inhibitors are observed. Therefore, for metal based anticancer agent, development of inhibitors with strong specificity, low toxicity and isoform selectively can be the future scope in this field. During the literature study it is observed that metal-based inhibitor expressed their inhibitory activity by coupling with known organic inhibitors, but the metal moiety itself has difficulty in their activity. Hence, we can say that it is also a scope for new inorganic chemists to develop simple metal complexes to exert enzyme inhibitory activity.

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AGRICULTURAL WASTE: GENERATION AND MANAGEMENT

A Short Review

Submitted for partial fulfilment of the B. Sc. degree in Chemistry

By

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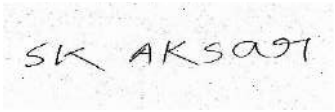

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ABSTRACT

Agriculture plays a vital role in world economy. Over 58% rural households depends on the agriculture. In recent years agriculture and allied areas has been facing the challenges. Agricultural waste is non-product output of production and processing of agricultural products that may contain material that can be beneficial for human being. Generally, the agricultural wastes are generated from number of sources such as cultivation, livestock, Industrial means, etc. These types of wastes can be used for number of applications. Agricultural wastes produced by these number of ways are a great concern because of the problems of environmental pollution, rural sanitation, recycling and utilization. The present review aims to give the information on utilization of agricultural wastes into number of applications like biogas, bio-hydrogen, bioethanol, bio-fertilizers etc.

Keywords: *Agricultural waste, generation, utilization.*

1. INTRODUCTION

Agricultural wastes are defined as the residues from the growing and processing of raw agricultural products such as fruits, vegetables, meat, poultry, dairy products, and crops. They are the non-product outputs of production and processing of agricultural products that may contain material that can benefit man but whose economic values are less than the cost of collection, transportation, and processing for beneficial use. Their composition will depend on the system and type of agricultural activities and they can be in the form of liquids, slurries, or solids. Agricultural waste otherwise called agro-waste is comprised of animal waste (manure, animal carcasses), food processing waste (only 20% of maize is canned and 80% is waste), crop waste (corn stalks, sugarcane bagasse, drops and culls from fruits and vegetables, prunings) and hazardous and toxic agricultural waste (pesticides, insecticides and herbicides, etc). Estimates of agricultural waste arising are rare, but they are generally thought of as contributing a significant proportion of the total waste matter in the developed world. Expanding agricultural production has naturally resulted in increased quantities of livestock waste, agricultural crop residues and agro-industrial by-products. There is likely to be a significant increase in agricultural wastes globally if developing countries continue to intensify farming systems. It is estimated that about 998 million tonnes of agricultural waste is produced yearly [1]. Organic wastes can amount up to 80 percent of the total solid wastes generated in any farm [2] of which manure production can amount up to 5.27 kg/day/1000 kg live weight, on a wet weight basis [3].

2. AGRICULTURAL WASTE GENERATION

As earlier noted, agricultural development is usually accompanied by wastes from the irrational application of intensive farming methods and the abuse of chemicals used in cultivation, remarkably affecting rural environments in particular and the global environmental in general. The waste generated is dependent on the type of agricultural activities carried out

2.1. Wastes from Cultivation Activities

While tropical climate is favorable for growing crops, it also supports the generation and development of insects and weeds. This situation creates a high demand for pesticides in order to kill insects and protect against the spread of epidemic diseases; this need often lead to the abuse of pesticides by farmers. After using pesticides, most of the bottles and packages holding these pesticides are thrown into fields or ponds. According to an estimate made by the Plant Protection Department (PPD), about 1.8% of the chemicals remain in their packaging .These wastes have the potential to cause unpredictable environmental consequences such as food poisoning, unsafe food hygiene and contaminated farmland due to their potentially lasting and toxic chemicals. In addition to this, existing stagnant or unused pesticides and pesticide packages with residue from the original contents poses serious environmental consequence in that they could be stored or buried in the wrong way which may leak or enter the environment through osmosis and thereby affecting the environment. In agricultural production for example, fertilizers play an important role in maintaining the productivity and quality of plants. Inorganic fertilizer is inexpensive and characterized by high productivity. However, many farmers apply more fertilizer to their crops than the amount needed by the plants.

2.2. Wastes from Livestock Production

Waste from livestock activities include solid waste such as manure and organic materials in the slaughterhouse; wastewater such as urine, cage wash water, wastewater from the bathing of animals and from maintaining sanitation in slaughterhouses; air pollutants such as H_2S and CH_4; and odours. The pollution caused by livestock production is therefore a serious problem since most of them are usually built around residential areas. Air pollution includes odours emanating from cages resulting from the digestion process of livestock wastes; the putrefaction process of organic matter in manure; animal urine, and/or from redundant foods. The intensity of the smell depends on animal density, ventilation, temperature, and humidity. The proportion of NH3, H2S, and CH4 varies along with the stages of the digestion process and also depends on organic materials, the components of foods, microorganisms, and the status of the animals' health.

2.3. Waste from Aquaculture

The growth in aquaculture has led to an increase in the use of feeds for improved production. The amount of feed used in a system is the most important factor used in determining the quantity of waste generated. The wastes that result from the use of aquaculture feeds are discussed in this section of the report and it is a summary of the information provided by [7]. One of the major wastes generated in aquaculture is metabolic waste which could be dissolved or suspended. In a properly managed farm, approximately 30% of the feed used will become solid waste. Feeding rates are dependent on the ambient temperature. Increase in temperature results in increased feeding which gives rise to increased generated waste. Water flow patterns in production units are important for waste management because a proper flow will minimize the fragmentation of fish faeces and allow for rapid settling and concentration of the settleable solids. This can be critical because a high percentage of non-fragmented faeces can be quickly captured which will greatly reduce the dissolved organic waste [8].

3. WASTE UTILIZATION ROUTES

Agricultural waste utilization technology must either use the residues rapidly, or store the residues under conditions that do not cause spoilage or render the residues unsuitable for processing to the desired end product [8]. These wastes can be utilized by number of ways for number of applications which includes:

3.1 Fuel

The fuel such as petrol, diesel, kerosene etc are nonrenewable sources of energy as they are produced by the decomposition of fossils under the earth. These types of resources are being exhausted because of increase in population and rapid urbanization which will affects the earth's atmosphere by polluting the air by burning of fuels. Because of these there is a need to find the alternative source for the fossil fuels. The agricultural waste can be converted into the fuel to fulfill our daily requirements. The agro-wastes can be utilized for Biogas, Bioethanol, Bio-hydrogen, and Biobutanol.

3.2. Bioethanol

Increase on world's energy demand and the progressive depletion of oil reserves motivate the search for alternative energy resources, especially for those derived from renewable materials such as biomass [9]. In its simplest form, bioethanol is the alcohol produced from the starchy material with the help of microorganisms by the process called fermentation. The ethanol is then concentrated and recovered in the process called distillation. Ethanol production represents an effective method for conversion of biomass into liquid fuel, as a way to replace or supplement our reliance on fossil fuels. There are two types of microbes, one is aerobic and another is anaerobic. In ethanol production generally anaerobic microbes are used. Primarily the yeast namely Saccharomyces cerevisae is used for this purpose the starch hydrolysis by enzyme includes two stages i.e., liquefaction and saccharification. In liquefaction the starch is degraded or hydrolyzed into dextrins by the action of endoacting enzyme namely α-amylase. The dextrins obtained after liquefaction, is further hydrolyzed to glucose by glucoamylase. Glucose is then converted to ethanol by yeast fermentation. By the end of fermentation, the obtained product is subjected to distillation to remove water, and other impurities, yielding pure ethanol. Glycolysis is the normal pathway for breakdown of glucose in most of organisms. Under the aerobic conditions the end point of glycolysis is pyruvate, while under anaerobic conditions the end point is ethanol.

3.3. Biogas

Interest in biogas technology is increasing around the world due to the requirements for renewable energy production, reuse of materials and reduction of harmful emissions. It produces methane-rich biogas which can be utilised as renewable energy in various ways. Biogas technology is currently the most sustainable way to utilise the energy content of agro-waste while also recycling the nutrients and minimising the emissions. Biogas is also known as anaerobic digestion which plays an important role in manure treatment processes. It includes number of biochemical processes by different microorganisms to degrade organic matter under anaerobic condition. The byproduct of anaerobic digestion (Methane) is a rich source of renewable energy, which can replace fossil fuel. Biogas contains mainly methane (55-70%), while the rest is mostly carbon dioxide. Small quantities of other gaseous compounds such as hydrogen, hydrogen sulphide, ammonia, oxygen, nitrogen, silicon dioxide and particulates are also present depending on process

technology and the raw materials digested. The degradation of organic matter to biogas is a very complex process which includes hydrolysis, acidogenesis, acetogenesis and methanogenesis.

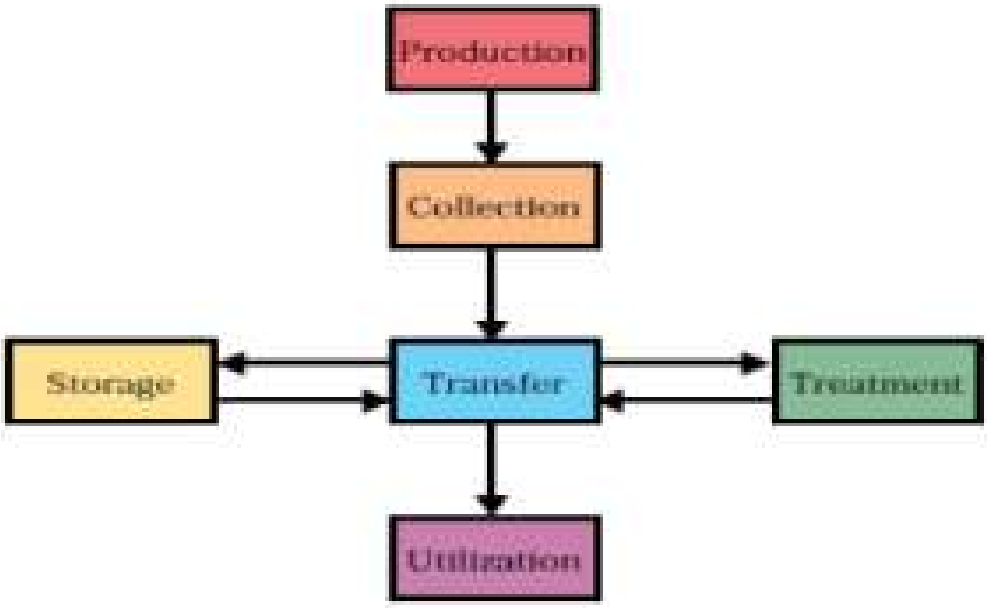
3.4. Biofertilizer

"Biofertilizers" are those substances that contain living microorganisms and they colonize the rhizosphere of the plant and increases the supply or availability of primary nutrient and/or growth stimulus to the target crop [15]. The utilization of animal manures for fertilizer has a great impact on input energy requirements at the farm level. Manure could supply 19, 38 and 61% of nitrogen, phosphorus and potassium in fertilizer [16]. Addition of manure to soil increases its fertility because it increases the nutrient retention capacity, improves the physical condition of soil, the water-holding capacity and the structure stability of soil. Biofertilizers are made from easily obtained organic materials such as rice husk, bamboo, vegetable wastes, molasses etc that can be found in even the most remote areas. Biofertilizers are environment friendly substitute for harmful chemical fertilizers. They transform organic matter into nutrients that can be used to make plants healthy and productive. They have a low production cost because it produced from easily obtained organic matter.

4. AGRICULTURAL WASTE MANAGEMENT SYSTEM (AWMS)

Recently, agricultural waste management (AWM) for ecological agriculture and sustainable development has become an issue of concern for policy makers. The usual approach to agricultural waste management has been discharge to the environment with or without treatment. There is need to consider wastes as potential resources rather than undesirable and unwanted, to avoid contamination of air, water, and land resources, and to avoid transmission of hazardous materials. This will require better use of technology and incentives, a change in philosophy and attitudes, and better approaches to agricultural waste management. The organic wastes, especially manure generated by animals, if improperly managed or left untreated can result in significant degradation of soil, water and air quality. Stagnant wastes provide a medium in which flies breed and diseases are transmitted. Uncontrolled decomposition of organic wastes produces odorous gases as well as ammonia volatilization, leading to acid rain. Because of the intensification of animal production on a small area of land, there are increasing concerns about: • Water quality resulting from higher nitrogen and phosphorous loadings; • Pathogens and antimicrobial

compounds in the manure; • Foul odors and air quality from ammonia, methane and nitrous oxide emissions; • Soil quality because of potassium and phosphorous loading. An Agricultural Waste Management System (AWMS), according to is a "planned system in which all necessary components are installed and managed to control and use bye products of agricultural production in a manner that sustains or enhances the quality of air, water, soil, plant, and animal resources". Such a system is developed using total systems approach, i.e. it is designed to cater for all the waste associated with agricultural production to utilization throughout the year round.



Scheme 1: Agricultural Waste Management Functions

The Total Solids (TS) concentration of agricultural wastes is the main characteristic that determines the handling of the material. For excreted manure for example, the following factors affect the TS concentration and they include the climate, type of animal, amount of water consumed by the animal, and the feed type. In most systems the consistency of the waste can be anticipated or determined. The TS concentration of the waste can be increased by adding beddings or other solid waste to the waste, decreased by adding water, and stabilized by protecting it from additional water. The TS concentration is important in that it affects the total volume of the waste to be handled. Liquid waste management systems are often easier to automate and manage than

those for solid wastes; however the initial cost of the liquid handling equipment may be greater than that for solid waste systems.

5. CONCLUSION

Agricultural wastes are residues from the growing and processing of raw agricultural products. These types of products are non-product outputs of production and processing which may contain material that can benefit human. These residues are generated from a number of agricultural activities such as cultivation, livestock production and industrialization. These wastes can be managed properly through the number of applications such as fuel, fertilizers, animal feed etc. Proper waste utilization will assist in developing our agricultural sector and provide viable biofertilizers and biofuel resource for many.

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A Review

ON

Effectiveness of Copper against viruses like Covid-19 virus

Project Work

Submitted for partial fulfillment of the B.Sc (Honours) Degree in Chemistry

By

Soumadeep Sur

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Registration Number - A01-1112-112-013-2019

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Acknowledgements

I gratefully acknowledge our respected Principal Maharaja for giving us inspiration and motivation. I am grateful to my advisor, **Dr. Tapas Ghosh,** Associate Professor, Department of Chemistry, Ramakrishna Mission Vivekananda Centenary College,Kolkata-700118 for his guidance on the related area of this project work and continuous support.

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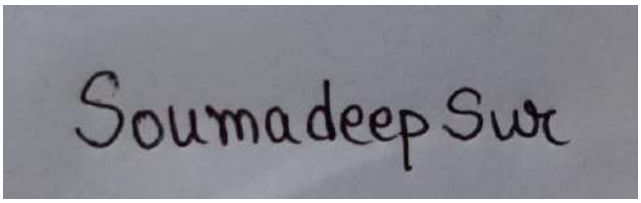

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Date:- 15/01/2022

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Effectiveness of Copper against viruses like Covid-19 virus

ABSTRACT

Copper and its alloys are prospective materials in fighting covid-19 virus which has been severely affecting the world for 2 years as a global pandemic. Also they can help in fighting several microbial pandemics due to its antiviral and antimicrobial properties. Several studies have been conducted on copper and its alloys and it has been proven that they have the potential in controlling the spread of infectious diseases. Also recent studies indicate that these alloys can effectively inactivate covid-19 virus. In this project, the antimicrobial properties of copper and its alloys have been discussed and also how they reduce the spread and infection of covid-19 in detail.

INTRODUCTION

Coronavirus or Covid-19 is a contagious viral disease caused by severe acute respiratory syndrome coronavirus 2 (SARS-CoV-2). The first known case of Covid-19 was reported in 1st December 2019 in Wuhan, China and since then the disease has spread worldwide leading to an ongoing pandemic.

Covid-19 spreads via droplets or small airborne particles containing the virus which are released into the air when an infected person breathes, coughs and sneezes. Thus it can spread when people are in a large gathering and thus it is essential to wear masks,

maintain physical distance and keeping our hands regularly sanitized. A person can also be indirectly infected when he comes in contact with an object contaminated by the droplets and it can be controlled by minimizing life expectancy of the virus on the contaminated surfaces by developing efficient surface technologies for virus inactivation. Here we will discuss how on copper surfaces, viral growth and microbial growth are affected.

History of Copper in Medicine

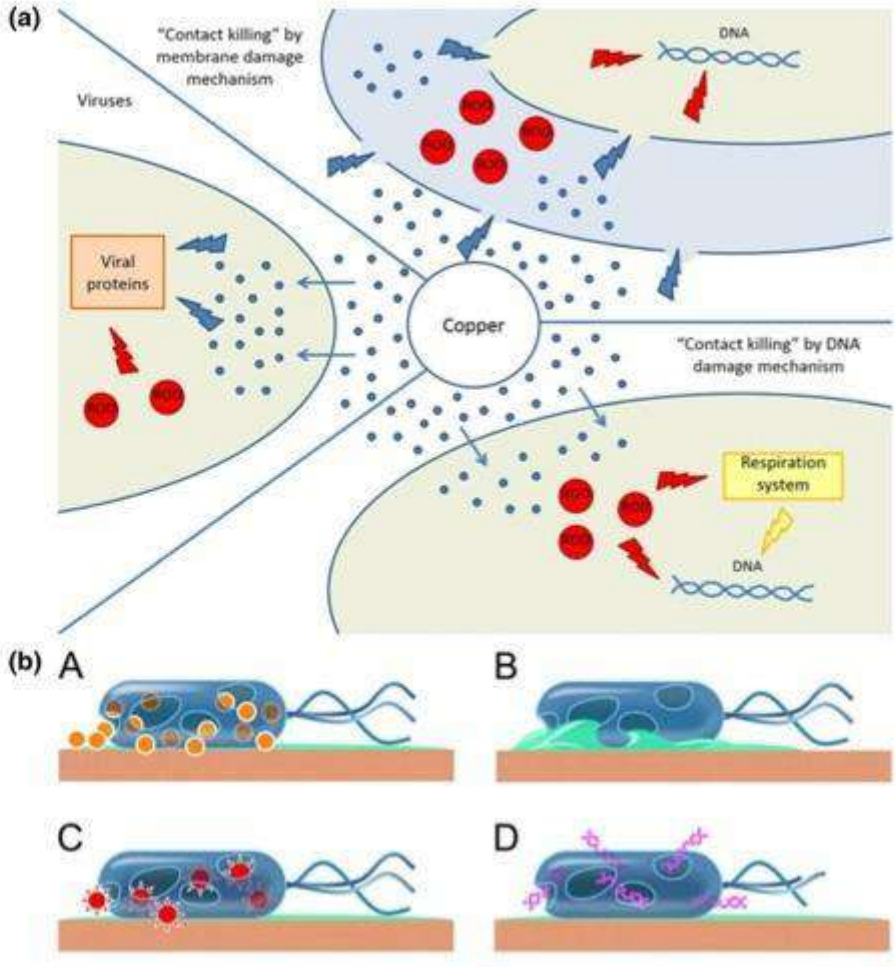
Copper has antimicrobial and antiviral properties and it is a huge boost to our immune system. Surfaces containing copper and its alloys can inactivate viruses. It has been of great importance since the ancient civilizations. In Egyptian civilization it was used for water sterilization. It was used by Romans to cure headache and infection in ear. In Greece it was used for treatment of ulcerations. In ancient India also, Copper was used for treatment. Use of Tamra Patra is recorded in Charaka Samhita. In the 19th and 20th Century, it was greatly used for treatment of various diseases like syphilis, anaemia, cholera, eczema etc. Researchers have shown that treatment using copper is better than Iron Therapy.

Effect of Copper Content in Human Body

Copper is an important nutrient for our body. It helps in digestion and plays a vital role in Iron metabolism. According to researchers, the daily intake of copper must be of about 2.6 mg. However if we don't intake copper regularly then deficiency of copper can occur which can result in abnormalities in various systems such as cardiovascular, pulmonary neuronal, skeletal, immunology and behavioral functions in offspring during infancy and beyond may appear. Copper plays an important role in functioning of B cells, T helper cells, natural killer cells, neutrophils and macrophages which are essential immune cells thus deficiency of copper leads to weakened immune response leading to parasitic infections.

Antiviral Mechanism of Copper

Copper's toxic properties make it a powerful antimicrobial agent. It's ability to generate ROS (Reactive Oxygen Species) makes it toxic. By exposing the pathogens to copper toxins, the virus particles can be reduced on copper surfaces. Copper ion binding and cross-linking between the strands of genome can damage the viral genomic DNA. As DNA is a potential target for cytostatic drugs, when copper is used, Copper (ll) complexes bind with DNA generating ROS which leads to degradation of DNA. Also by degrading the genomic and plasmid DNA, it can destroy microbes.
Microbes can't stay for much time on copper surfaces as copper ions destroy them via contact killing process. In this process it causes cell damage after which the cell membrane gets ruptured inducing loss of cytoplasm in the cell. Also the copper ions generate ROS which further damage the cells.



The figure (a) shows the contact killing Mechanism of copper against bacteria (top),

virus (middle) and fungus (bottom). (b) Illustration of contact killing mechanism on a copper surface (A) rupture of cell membrane (B) loss of cytoplasmic content (C) generation of other ROS by copper ions and (D) degradation of DNA

When a virus is exposed to copper surface, the viral nucleic acid degrades due to the copper ions. Researchers have found that Cu(ll) ions inactivated five enveloped or non-enveloped, single or double stranded DNA or RNA viruses. Addition of peroxide acted as a catalyst. Comparing with iron(lll), after addition of peroxide, copper peroxide acted as more effective antimicrobial agent against Herpes and Junin simplex viruses. The viral genomes were disrupted by copper ions and the morphology of virus was irreversibly changed inducing the disintegration of envelope and the dispersal of surface spikes. Inactivation was triggered by Cu(l) and Cu(ll) ions aided by ROS generation leading to even faster inactivation as compared to non-enveloped viruses. Compared to other materials, Copper surfaces shows decrease of 83 percent of microbes contamination. Copper containing materials such as brass containing greater than 70 percent copper exhibits superior virucidal action on HuCoV-229E compared to other materials like stainless steel, Teflon, PVC, glass and ceramics. Also the amount of virus to remain in the surface was proportional to the amount of copper in the alloy further establishing it's effectiveness. Doctors and medical workers are always at the risk of getting infected as they regularly come in contact with the viruses so they should use copper solutions to prevent the indirect transmission. Also if covid-19 virus is exposed to copper on surface then it shows rapid inactivation, irreversible viral RNA destruction and severe structural damages.

Copper based alloys

We have already shown how copper and it's alloys exhibit superior virucidal action in comparison to other materials. They are effective on Herpes simplex, HIV-1, bronchitis, hepatitis-C, poliovirus, monkey pox and covid-19 by damaging the biomolecules, RNA, DNA, genome and protein shell. Inactivation of bacteria and viruses on copper can take variable time depending upon whether the pathogen is

gram-positive or gram-negative bacteria or enveloped or non-enveloped viruses. In case of pure copper metal, Murine Norovirus (MNV) was not present after 30 mins and for copper-nickel alloy it was after 60 mins and it is temperature dependent. It was observed via scanning electron microscopy images that copper could inhibit the bacteria adhesion and decrease biofilm development. Also another copper based material, calcined copper called as "Tamra bhasma" has been said to be effective in the fight against microbes in Ayurveda.

Application of copper based materials

Copper alloys must be used in public spaces on common touch surfaces, especially where there is a lot of human traffic to prevent indirect transmission. Nowadays,

copper is used as a surface disinfectant and also regularly in the pharmaceutical industry. The figure above shows various applications of copper based materials.

Copper based Nanomaterials

Nanotechnology has enabled distinctive possibilities to solve a wide range of problems. Nanoparticles (NPs) having diameter of less than 100nm have medical properties, used in drug synthesis and therapeutics. In comparison to particles from same material, NPs have a higher surface to volume ratio, making them more reactive and thus have improved interaction with microbes and so have increased antimicrobial properties. Due to high surface area they have higher killing efficiency and can induce cytotoxicity in microorganisms.

Metal NPs can stop viral replication and propagation, causes viral inactivation and induce virucidal effects by blocking entry of virus in the cells. Metal NPs can destroy the outer layer of covid-19 virus.

Copper based NPs are used in wound dressings and its iodide, oxide and sulphide forms show antiviral activity against herpes simplex virus, human norovirus and H1N1 Influenza virus. They also possess anti-parasitic and anti-cancer qualities. CuO-NPs reduce virus population and exhibit strong antiviral activity against HSV-1. It also possess antibacterial action against gram-positive and gram-negative bacteria. They are also used in antifouling paints, agricultural biocides, wood preservation. CuI NPs display antiviral activity against Influenza virus. They are also used in face masks, filters, kitchen cloths. Tamra Bhasma has anti-inflammatory properties and exhibits virucidal action against covid-19.

Copper based Coating Technologies

Bulk components can be replaced by copper based materials. Cold spray technique is an effective method to deposit copper on surfaces leading to improved virucidal action against covid-19 virus. Covid-19 can also be inactivated by Cyta-Coat which is the primary antimicrobial covering made with biocompatible organic components. It can

be applied in face masks. Apart from it, thermal spray technique based on wire-arc spraying of copper has also been used. In hospitals of Canada and Peru, twin arc type thermal sprayed CuNiZn based copper alloy coatings are applied on chair arms, cabinet handles, charting tables and push plates/handles for doors.
Effective antimicrobial activity is exhibited by Cu-Ag coatings. The improved bacterial resistance is explained by the factors like (a) bacterial cell oxidation due to galvanic coupling induced redox reaction (b) copper ion release and (c) localized rise in pH. The surface displayed biofilm eradication of gram-positive bacteria in shorter time in comparison to gram-negative bacteria.

Limitations

Although it has excellent antiviral properties, copper based materials have some limitations. For humans, Copper is essential for intake in moderate levels but excess or deficiency of it can affect our health. So we have to be cautious about the amount of copper we intake. Also copper is expensive and harder to clean without causing erosion, so it's use in medical applications is limited. And on exposure of air, copper undergoes rapid oxidation which reduces its antimicrobial use in aerobic condition.

Conclusion

Thus copper based materials help us to inactivate Covid-19 virus. They have antimicrobial properties and antiviral properties. It can inactivate them by contact killing thus changing the virus morphology, envelope disintegration and dispersal of surface spikes. On copper surfaces, the covid-19 virus is active for less than 4 hours whereas in plastic and stainless steel it stays for more than 30 days. Thus copper alloys must be used in common touching surfaces such as doorknobs, stair railings, push plates, handles, electrical switch plates etc. By this way we can prevent the indirect transmission of covid-19 virus.

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Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit

Project Work

Submitted for partial fullfillment of the B.Sc. Degree in Chemistry

By

Soumyadip Parya

Under the supervision of Dr. Bipul Mondal

Soumyadip Parya

Reg. No.- A01-1112-112-012-2019

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Date: 15/01/2022

Place: Rahara

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To Whom it may concern

This is to certify that the project entitled "Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit" is the result of review work done by Mr.Soumyadip Parya , who has registered his name in "Ramakrishna Mission Vivekananda Centenary College (Autonomous), Rahara, Kolkata-700118, in undergraduate level. This work has been carried out under my supervision in this college.

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Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit

ABSTRACT

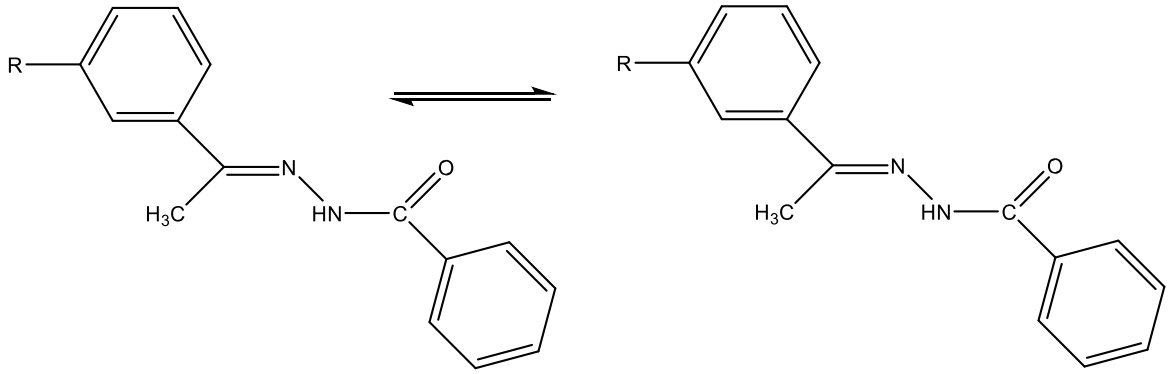
Dinuclear trioxidic [$(VOL)_2\mu$-O] (1-4) complexes were synthesized from the reaction of [$VO(acac)_2$] with an equimolar amount of H_2L [H_2L is the general abbreviation of hydrazone ligands (H_2L^{1-4}) in which the two H's representing the dissociable phenolic and amide protons, derived from the condensation of benzoyl hydrazine with either 2-hydroxyacetophenone or its para substituted derivatives] in acetone or dichloromethane or acetonitrile. These $V_2O_3L_2$ complexes were also obtained from the reaction of $VOSO_4$ with H_2L in the presence of two equivalents sodium acetate in aqueous-methanolic (50% V/V) medium and also from the decomposition of [$V^{IV}O(L)$(bipy/phen)] complexes in CH_2Cl_2 solution. Black monoclinic crystals of 2 and 4 with C2/c space groups were obtained from the reaction of [$VO(acac)_2$], respectively with H_2L^2 and H_2L^4 in acetone in which the respective ligands are bonded meridionally to vanadium in their fully deprotonated enol forms.

These dinuclear complexes are converted to the corresponding mononuclear cis *dioxido* complexes $K(H_2O)^+[VO_2(L)]^-$ (5-8) and mixed ligand [VO(L)(hq)] complexes on rection with 2 equivalent KOH in methanol and 2 equivalents 8-hydroxyquinoline in chloroform. Ascorbic acid reduces the dioxovanadium(V) complexes reversively under aerobic condition.

INTRODUCTION

Vanadium is an interesting transition element is relatively abundant (~ 0.015% of earth's crust) in nature and is present in plant and animal cells [1] at concentration 10-20 nM. Among the wide range of possible oxidation state -III to +V, Vanadium easily switches between +IV and +V and the stabilization of either of these two states under aerobic condition depends upon the basicity of the coordinated ligand and also on the pH of the reaction medium. The +V state has received considerable attention probably due to its two important properties: (i) it can exist in three motifs *viz*., mononuclear VO^{3+} and VO_2^+ motifs and dinuclear $V_2O_3^{4+}$ motif and (ii) it could exist in either 5 or 6 coordinated environment. These motifs are stable in solution around the physiological pH(~7) only when the metal is coordinated with sufficiently strong ligand for preventing the precipitation of hydroxides. The objectives of this

review: (i) to synthesize the complexes containing $V_2O_3^{4+}$ core with a family of hydrazone ligands, (ii) To study the various synthetic routes for the formation of such type of complexes, (iii) To examine the feasibility of conversion of these dinuclear complexes into the mononuclear complexes with VO^{3+} and VO_2^+ motifs and (iv) to study the electronic effect of para substituents in the hydrazone ligands on the vanadium in these complexes. Here the four tridentate dibasic hydrazone ligands H_2L^{1-4}, have been used, derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone and its para-substituted derivatives.



R	H_2L
H	H_2L_1
CH_3	H_2L_2
OCH_3	H_2L_3
Cl	H_2L_4

Fig. 1

SUMMARY OF THE PROJECT WORK Synthesis of H_2L^{1-4}

These hydrazone ligands derived by the condensation of benzoyl hydrazine with 2hydroxyacetophenone and its 5-substituted derivative [2,3] in methanol. In the free state, these are present in their keto-form but they undergo complexation through their completely enol form as indicated by their IR and ^{1}H NMR spectra.

Synthesis of the complexes $[V_2O_3L_2]$ (1-4)

All dinuclear trioxide $[V_2O_3L_2]$ complexes were synthesized by different methods using various starting materials, *viz*., (i) equimolar amount of $[V^{IV}O(acac)_2]$ and H_2L under refluxing condition in non-hydroxylic solvent [3] e.g., acetone, CH_2Cl_2, acetonitrile etc.; (ii) by reacting $VOSO_4$ with equimolar amount of H_2L in presence of two equivalents sodium acetate in aqueous-methanolic medium [3] and (iii) by the decomposition [4] of $[V^{IV}O(L)(bipy/phen)]$ complexes in non-hydroxylic solvent like CH_2Cl_2, $CHCl_3$, C_6H_6 etc. In

all the above methods the starting materials are different tetravalent precursors, and the oxidizing agent is most likely the aerial dioxygen. These reactions are represented by the following equations 1, 2, 3:

$2[V^{IV}O(acac)_2] + 2H_2L + ½O_2 \rightarrow [V^{V}{}_2O_3L_2] + 4Hacac$ - - - - - - - - - - (1)

$2VOSO_4 + 2H_2L + 4CH_3COONa + ½O_2 \rightarrow$

$[V^{V}{}_2O_3L_2] + 2Na_2SO_4 + 4CH_3COOH$ - - - (2)

$2[V^{IV}OL(bipy/phen)] + ½O_2 \rightarrow [V^{V}{}_2O_3L_2] + 2(bipy/phen)$ - - - - - - - -- (3)

Where Hacac, bipy and phen are representing respectively acetylacetone, 2,2′bipyridine and 1,10-phenanthroline.

Monoclinic crystals of $[V_2O_3(L^2)_2]$ (Fig. 2) and $[V_2O_3(L^4)_2]$ (Fig. 3) with *C2/c* space group were obtained by following the above-mentioned preparative method (1), while orthorhombic crystals of $[V_2O_3(L^2)_2]$ (Fig. 4) with *Pbca* space group were obtained by adopting the preparative method (3). The analytical, spectral (IR, UV-vis and 1H NMR) and electrochemical data of these two dimorphs are identical (within experimental error). The solid-state structural features of these dimorphs differ in crystal packing and in the molecular symmetry. In the monoclinic variety, two structurally very similar but crystallographically distinct respective molecules are present in both the crystal lattices of $[V_2O_3(L^2)_2]$ and $[V_2O_3(L^4)_2]$ with the bridging oxygen lying on a crystallographic 2-fold axis such that the two halves of each of the two molecules are crystallographically equivalent while in the orthorhombic variety of $[V_2O_3(L^2)_2]$, discrete molecules constitute the crystal lattice and the bridging atom has no crystallographic symmetry but two halves of the molecule have closely matching dimensions. However, in both varieties the geometry at metal center is a distorted square-pyramid with the meridionally disposed respective hydrazone ligand in enol form. The bridging oxo-oxygen occupies the fourth position of the square plane and the terminal oxooxygen is occupied in one of the two axial positions. The two terminal oxygen atoms O(1) and O(1)$1 (for the crystals with *C2/c* space group) or O(1) and O(1a) (for the crystals with *Pbca* space group) are mutually *trans* lying on opposite sides of the V−O−V plane. The extent of distortion is different for each of the vanadium centers even within the same structure. The V-O bond lengths follow a general order: $V-O^t$ (t = terminal) < $V-O^b$ (b = bridging) < $V-O^p$ (p = phenolic) < $V-O^e$ (e = enolic). The V−O−V angles are very similar and are close to 113º, which is consistent with the reported values of analogous hydrazone complexes [5, 6, 7].

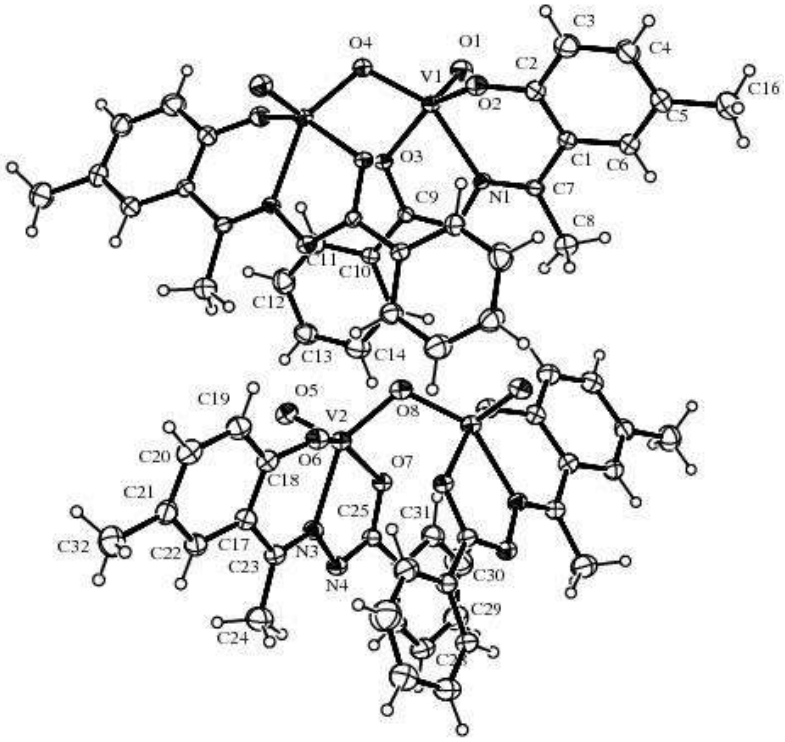


Fig. 2: Molecular structure of $[V_2O_3(L^2)_2]$ (with *C2/c* space group) with thermal ellipsoids drawn at 50% probability.

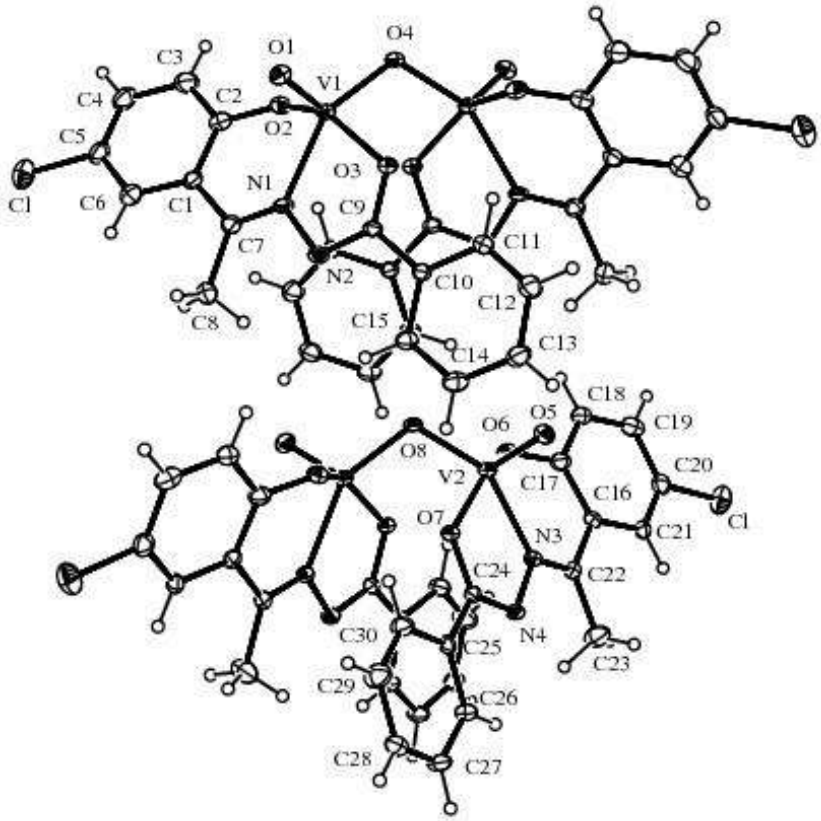


Fig. 3: Molecular structure of $[V_2O_3(L^4)_2]$ (with *C2/c* space group) with thermal ellipsoids drawn at 50% probability.

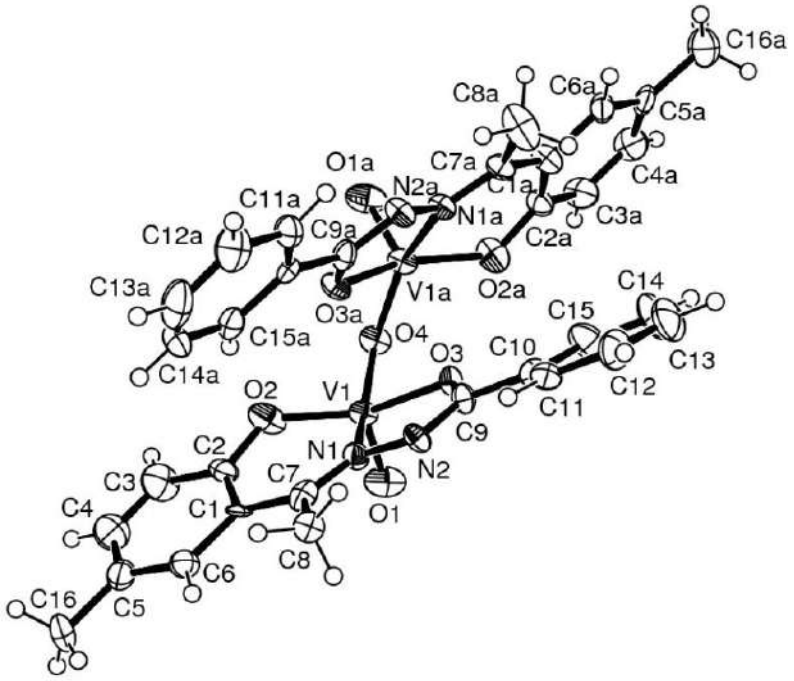


Fig. 4: Molecular structure of $[V_2O_3(L^2)_2]$ (with *Pbca* space group) with thermal ellipsoids drawn at 50% probability.

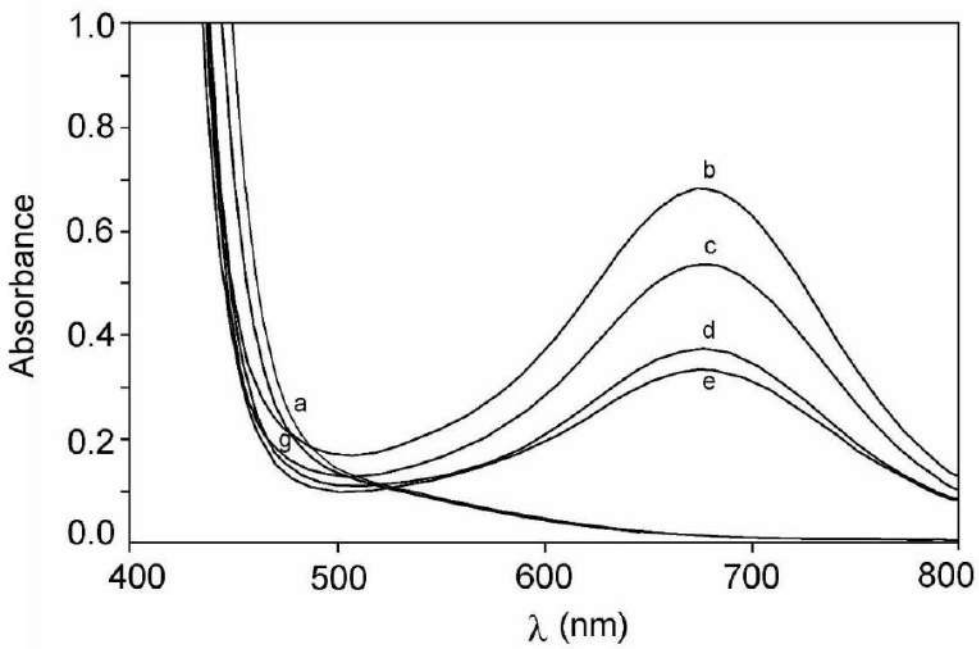


Fig. 5: Electronic spectra (400-800 nm) of a 7.973×10^{-4} mol dm^{-3} methanol solution of complex $K(H_2O)^+[VO_2L]^-$: (a) before the addition of ascorbic acid, (b) immediately after the addition of ascorbic acid, (c) 15 min after the addition of ascorbic acid, (d)

40 min after the addition of ascorbic acid, (e) 80 min after the addition of ascorbic acid and (f) 720 min after the addition of ascorbic acid. The concentration of ascorbic acid was about 10 times than that of the concentration of the complex.

Conversion of $[V_2O_3L_2]$ complexes to $K(H_2O)^+[V^VO_2L]^-$ and $[V^VOL(hq)]$ complexes

These dinuclear oxidovanadium(V) complexes can easily be converted to either mononuclear dioxidovanadium(V) complexes $K(H_2O)^+[V^VO_2L]^-$ or mixed-ligand complexes of the type $[V^VOL(hq)]$ on reaction, respectively, with two equivalents KOH in methanol and two equivalents 8-hydroxyquinoline (Hhq) in $CHCl_3$. The respective reactions are:

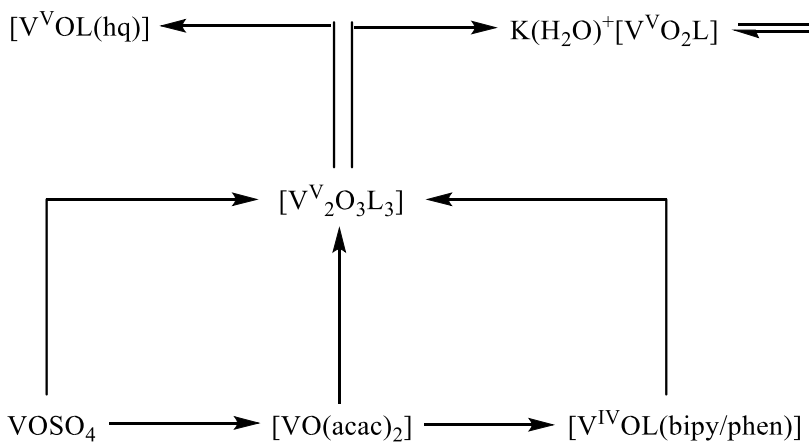
$$[V^V{}_2O_3L_2] + 2KOH + H_2O \rightarrow 2K(H_2O)^+[V^VO_2L]^-$$

$$[V^V{}_2O_3L_2] + 2Hhq \rightarrow 2[V^VOL(hq)] + H_2O$$

Catalytic oxidation reaction of $K(H_2O)^+[V^VO_2L]^-$ complexes with ascorbic acid The mononuclear dioxidovanadium(V) complexes oxidise ascorbic acid reversibly which was monitored spectrophotometrically. In each case after the addition of reducing agent a new band in the visible region near 675 nm was detected to a d-d transition of the resulting V(iv) species. After keeping the solution for sometime the intensity of the new band decreases gradually and finally the initial spectrum was obtained in a time interval ~ 12 hour. These observations strongly suggest that during the oxidation of ascorbic acid the dioxidovanadium(V) complexes are reduced by it to form the corresponding V(IV) complex presumably of the type $[VO_2(L)]^{2-}$ are not stable under this environment.

CONCLUSION

The four dinuclear trioxide Hydrazone complexes have been synthesized from various synthetic routes starting from different VO^{2+} precursors and these hydrazone ligands are very suitable for the stabilization of these motifs. The formation of these complexes from the decomposition of mixed ligand [VO(L)(bipy/phen)] complexes in CH_2Cl_2 solution indicates that these ligands have strong tendency for the stabilization of vanadium in its highest oxidation state(+V). These dinuclear complexes can be converted to the mononuclear binary complexes with VO_2^+ motif simply by increasing the (PH ~ 11) of the solution and mixed ligand ternary complexes with VO^{3+} motif by adding a monobasic bidentate strong chelating ligands. The dioxidovanadium(V) complexes can catalyze the reversible oxidation of ascorbic acid under aerobic condition which is biologically important particularly in relation to insulin enhancing activity.



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SUPRAMOLECULAR ORGANOCATALYSTS

Project work

Submitted as Partial Fulfillment of the B.Sc Degree in Chemistry

by

Soumyodip Mandal

Under the supervision of Dr. Kumar Ranabir Sur

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Registration no. A01-1112-112-020-2019

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Acknowledgement

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Date:-

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Abstract:

The use of small organic molecules as catalysts has gained increasing importance recently. These substances, the so-called organocatalysts. Organocatalysis is going to be an art in Synthetic Green Chemistry and synthesis manly stated to be used for accelerating the rate of chemical reaction with a substoichiometric amount of an organic compounds which does not contain a metal atom. This work intends to briefly show some classic works and recent publications,explaining the advantages of organocatalysis and the different types of compounds used in this field, as well as their course of action.

Introduction:

A catalyst is a substance that facilitates the course of a reaction without affecting its equilibrium position but decreasing the activation energy of the process.

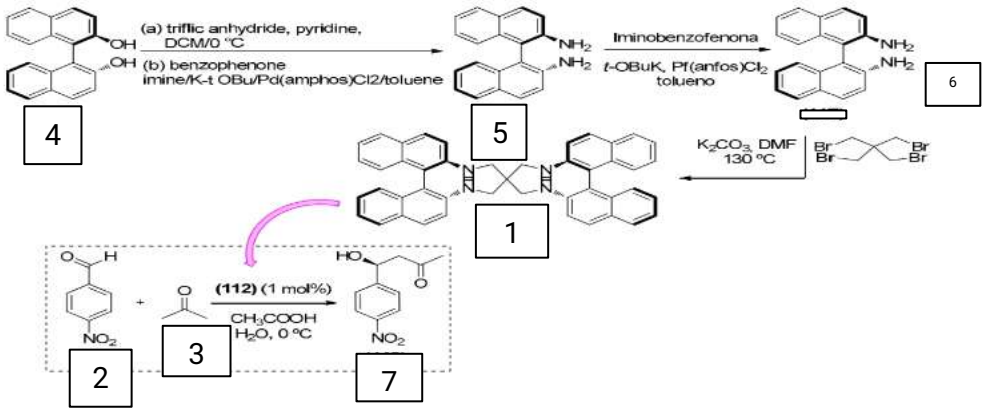
According to their chemical composition, catalyst can be metallic, enzymatic or organic. For some years the use of metallic catalyst is increased.

Organocatalysis is the use of small organic molecules to activate substances, which are electrophiles or nucleophiles.

Results and Discussion:

Now a days the use of organocatalyst is increased. Supramolcular organocatalyst act via hydrogen bonding and other interactions.

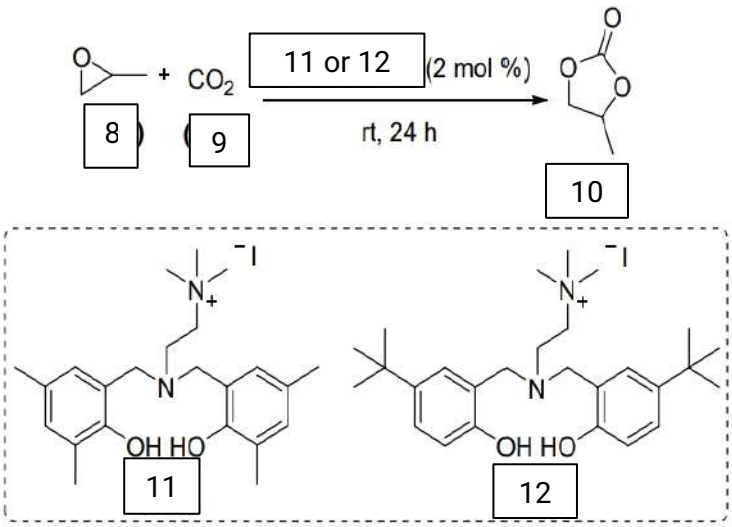
1) The compound (1) is synthesized by Ashokkarar et al. , which is an organocatalysts. This is used in 4-NO_2 - benzaldehyde(2) with ketones eg. acetone (3). Here the product is form 98% yeild. Here acetic acid donated H+ and forceing the acetone attack on the Si face of the aldehyde.



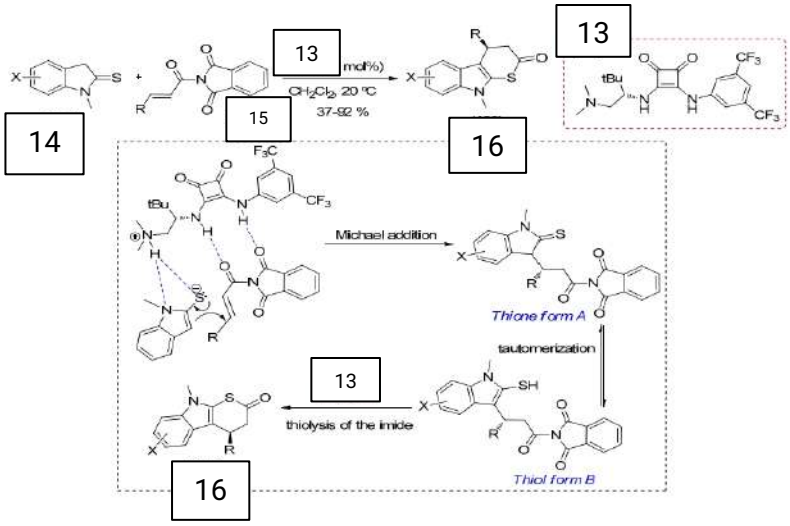
2) A series of organocatalysts was synthesized. These are applied in the cyclo addition between propylene oxide(8) and Carbon dioxide(9), giving propylene carbonate(10). This process fight against global warming. It contributes to the fixation of the atmospheric carbon dioxide.

(11) and (12) catalysts were the best ones for this process. With catalyst (11) giving propylene carbonate (10) is 85% yeild at 10 bar, 69% at 5 bar, 42% at 1 bar.

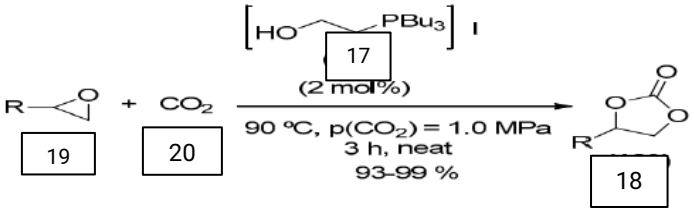
This catalyst helps to open the epoxide ring. This catalysts are recycled and used five times without loss of efficiency.



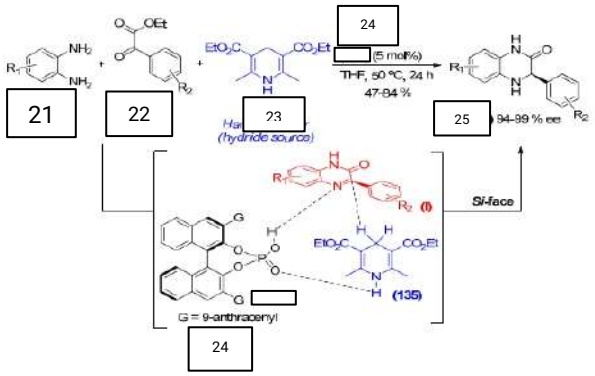
3) The bi-functional squaramide catalyst(13) derived from L-tert-leucine promoted the asymmetric tandem. Michael/thiolysis reaction sequence between 9-methylindoline-2-thiones(14) and N-alkenoylphthalimides(15) to furnish 3,4-dihydro-9-methylthiopyrano(16) in good yeilds and with high levels of enantioselectivity up to 98% ee.



4) Cyclic carbonates(18) from epoxides(19) and CO_2(20) is prepared with bifunctional phosphonium salts(17) as organocatalysts. In addition to the activation provided by the phosphonium salt moiety, there is a synergic effect of the hydrogen bonding arising from the terminal alcohol. By this catalyst, we get cyclic carbonates with excellent yeilds 93-99%. The catalyst could be recovered and reused upto five times.



5) The cyclization of 1,2-phenylenediamine (21) with ethyl 2-oxo-2-phenylacetate (22), giving intermediate product **I.** Next these product undergoes a enantio-selective transfer hydrogenation step using the Hantzsch ester (23) as a hydride source in the presence of a chiral phosphoric acid (24). By these process it gives the desired enantio-enriched product (25) in a step-economical overall process.



Conclusions:

There are many these type supramolecular organocatalyst which are used in several reaction. It employs mild conditions, consequently saving energy. In general, oxygen-stable reagents and does not require anhydrous conditions, reducing the cost of synthesis. It helps by lowering the total number of reaction steps. It prevents the formation of metallic waste and avoids traces of metals in the products, which is an essential feature for applications in medical Chemistry.

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GLOBAL SCENARIO OF AGRICULTARAL WASTE MANAGEMENT

A Short Review

Submitted for partial fulfillment of the B. Sc. degree in Chemistry

By

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[Registration No. : A01-1112-112-008-2019]

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Date:- 14-01-2022

Certified that the short review entitled "GLOBAL SCENARIO OF AGRICULTARAL WASTE MANAGEMENT" submitted by **Mr. Subhajit Pal** [Registration No.: A01-1112-112-008-2019] for the partial fulfillment for the B.Sc. degree in chemistry in Ramakrishna Mission Vivekananda Centenary College, Rahara has been executed under my guidance.

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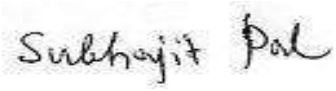

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ABSTRACT

Agricultural wastes are non-product outputs of production and processing of agricultural products that may contain material that can benefit man but whose economic values are less than the cost of collection, transportation, and processing for beneficial use. Estimates of agricultural waste arising are rare, but they are generally thought of as contributing a significant proportion of the total waste matter in the developed world. Agricultural development is usually accompanied by wastes from the irrational application of intensive farming methods and the abuse of chemicals used in cultivation, remarkably affecting rural environments in particular and the global environment in general. Generally, agricultural wastes are generated from a number of sources notably from cultivation, livestock and aquaculture. Agricultural waste has a toxicity potential to plant, animals and human through many direct and indirect channels.

Keywords: *Agricultural waste, generation, utilization.*

1. INTRODUCTION

The by-products of agricultural activities are usually referred to as “agricultural waste” because they are not the primary products. These wastes chiefly take the form of crop residues (residual stalks, straw, leaves, roots, husks, shells etcetera) and animal waste (manure). Agricultural wastes are widely available, renewable and virtually free, hence they can be an important resource. They can be converted into heat, steam, charcoal, methanol, ethanol, bio diesel as well as raw materials (animal feed, composting, energy and biogas construction and so on). However, many of the agricultural wastes are still largely underutilized. All these wastes are known to contain high nutrient levels of Nitrogen, Potassium, and Phosphorus that would improve soil fertility and increase crop yields such as vegetables, maize that fetch high prices and hence enhance food security. This alternate method of utilization by farmers for agricultural production has also reduced the rate of accumulation, with subsequent reduction on environmental pollution thus improving environmental health. This calls for a greater awareness of the public and farmers of the benefits of proper management and utilization of organic wastes in agriculture. This will lead to diminished fears and preconceived notions of nuisance problems that decrease land values and environmental degradation.

2. AGRICULTURAL WASTE GENERATION

As earlier noted, agricultural development is usually accompanied by wastes from the irrational application of intensive farming methods and the abuse of chemicals used in cultivation, remarkably affecting rural environments in particular and the global environmental in general.

2.1. Wastes from Cultivation Activities

While tropical climate is favorable for growing crops, it also supports the generation and development of insects and weeds. This situation creates a high demand for pesticides in order to kill insects and protect against the spread of epidemic diseases; this need often lead to the abuse of pesticides by farmers. After using pesticides, most of the bottles and packages holding these pesticides are thrown into fields or ponds. According to an estimate made by the Plant Protection Department (PPD), about 1.8% of the chemicals remain in their packaging .These waste have the

potential to cause unpredictable environmental consequences such as food poisoning, unsafe food hygiene and contaminated farmland due to their potentially lasting and toxic chemicals.

2.2. Wastes from Livestock Production

Waste from livestock activities include solid waste such as manure and organic materials in the slaughterhouse; wastewater such as urine, cage wash water, wastewater from the bathing of animals and from maintaining sanitation in slaughterhouses; air pollutants such as H_2S and CH_4; and odors.

2.3. Waste from Aquaculture

The growth in aquaculture has led to an increase in the use of feeds for improved production. The amount of feed used in a system is the most important factor used in determining the quantity of waste generated.

3. WASTE MANAGEMENT ROUTES

Agricultural waste utilization technology must either use the residues rapidly, or store the residues under conditions that do not cause spoilage or render the residues unsuitable for processing to the desired end product. There are a number of applications to which these wastes can be used. They include:

Fig 1: Conversion Of Agricultural Wastes Into Various Economic Resources

3.1 Fertilizer Application

The utilization of animal manures for fertilizer has a definite impact on input energy requirements at the farm level .nure could supply 19, 38 and 61% of nitrogen, phosphorus and potassium in chemical fertilizer .ever, fertilizer use of manures from large confinement is associated with high energy costs for transport, distribution, storage facility requirements, odour problems and possibility of groundwater contamination.

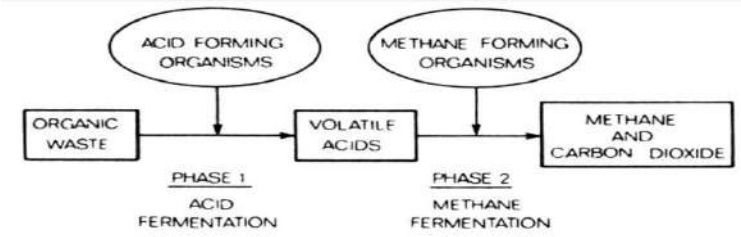

Fig 2: Methane Production By Two Stage Microbial Fermentation

3.2 Anaerobic Digestion

Methane gas can be produced from agricultural wastes particularly manures. The gas is best suited for heating purposes as in broiler operation, water heating, grain drying, etc. The anaerobic digestion of agricultural waste to form methane-rich gas is a two-step microbial fermentation. Initially, acid-forming bacteria break down the volatile solids to organic acids which are then utilized by methanogenic organisms to yield methane-rich gas.

3.3 Adsorbents in the Elimination of Heavy Metals

Excessive release of heavy metals into the environment due to industrialization and urbanization has posed a great problem worldwide. The low cost agricultural waste such as sugarcane bagasse, ice husk, raw dust, coconut husk oil palm shell, neem bark, etc., for the elimination of heavy metals from wastewater have been investigated by various researchers.

3.4 Pyrolysis

In pyrolysis systems, agricultural waste is heated up to a temperature of 400-600°C in the absence of oxygen to vaporize a portion of the material, leaving a char behind. This is considered to be a higher technology procedure for the utilization of agricultural wastes.

3.5 Animal feed

In most developing countries, the problem with animal feed is in the limited availability of protein sources although great efforts are being made to find alternative supplements. Crop residues have high fiber content and are low in protein, starch and fat. Therefore, the traditional method of increasing livestock production by supplementing forage and pasture with grains and protein concentrate may not meet future meat protein needs. Use of the grain and protein for human food will compete with such use for animal feed. These problems may be circumvented by utilizing residues to feed domesticated animals.

3.6 Direct combustion

The simple act of burning agricultural waste as fuel is one of the oldest biomass conversion processes known to mankind. Complete combustion of agro- waste "consists of the rapid chemical reaction (oxidation) of biomass and oxygen, the release of energy, and the simultaneous formation of the ultimate oxidation products of organic matter – CO_2 and water". The energy released is usually in the form of radiant and thermal energy provided oxidation occurs at sufficient rate; the amount of which is a function of the enthalpy of combustion of the biomass. Of all the processes that can be used to convert agricultural waste to energy or fuels, combustion is still the dominant technology accounting for more than 95% of all biomass energy utilized today.

4. AGRICULTURAL WASTE MANAGEMENT AROUND THE GLOBE

Agricultural wastes have become a matter of concern for everyone around the globe. It is still an unexplored matter for everyone. But researches are going everywhere around the globe where agriculture is being carried out on a large scale in order to properly manage the wastes and utilize them for the welfare of the country. The utilization of agricultural waste into usable products in agricultural major economies have been discussed below.

4.1. China

China is a traditional agricultural country with considerable amounts of poultry farms, crops and so on. With the development of agriculture in China, the productions of straw and livestock manure increase rapidly. It lacks laws and regulations of agricultural wastes recycling .The recycling and utilization pathway of agricultural wastes were analyzed. There were problems existing in the utilization process of agricultural wastes in China, which included the large quantity and unknown

amount of agricultural wastes. However, in modern agronomic process, the small-scale recycling utilization could not afford the amounts of agricultural waste produced rapidly. In the pre-experiment, rice nursery media is formulated by using pig manure, cow excrement, mushroom compost and inorganic minerals. The results showed that the basic media made of 55% organic fertilizers and 45% inorganic minerals for rice seedling growth were more suitable than 100% of pig manure, cow excrement, mushroom compost and inorganic minerals alone. Among media, the medium made of 35% pig manure, 20% cow excrement, 30% vermiculite and 15% perlite, gained the highest biomass and evenness. The seedling quality in media made of 60-70% organic fertilizer was better than the tested commercial media contained more than 80% organic fertilizer. The seedling quality in the media A and B were better than the other media. The media A was made of 30% pig manure, 30% cow excrement, 30% vermiculite and 10% perlite, whereas the media B, which was made of 20% pig manure, 30% cow excrement, 20% vinegar residue compost, 20% vermiculite and10% perlite. Nitro-humic acid and calcium superphosphate were added into nursery media, respectively. Seedling growth in the media with nitro-humic acid was better than that in the media with calcium superphosphate.

A series of measures were put forward (1) to establish and improve a lot of policies, laws and regulations related to the resourceful utilization and harmless disposal of agricultural wastes**,** (2) to increase the financial support from different channels and strengthen construction of basic infrastructures in agricultural waste utilization process by building a new countryside.

4.2. Pakistan

Pakistan has a major electricity supply problem with urban areas having a very intermittent supply of electricity. Pakistan has a large agricultural economic sector and produces a substantial amount of waste material that has little current economic use. Pakistan is one of the developing countries which are struggling hard to meet the demand for electric power generation. Pakistan currently relies on fossil fuel sources of energy that are expensive and bad for climate change. Renewable and sustainable biomass was shown to have the potential to generate 76% of the peak demand for electricity in Pakistan. Sugarcane, wheat straw, rice husk and maize are the main agricultural waste materials that could generate 56% of Pakistan’s electricity. Also it was shown that woody biomass could sustainably generate 9.5% of the peak demand for electricity. The remaining significant biomass resources were seed oils (Cottonseed, Rapeseed Mustard,

Sunflower and Canola) that could generate 8.2% of electricity. Banana trees that are widely spread in southern areas of Pakistan could generate 2.4% of electricity.

4.3. Nigeria

Rapid development in Nigeria is creating a shortage of building construction materials due to the inadequate availability of natural resources. Conversely, the energy consumed to produce building materials pollutes the air, water and land. To meet the increasing demand in sustainable building materials, the adoption of cost-effective, naturally appropriate technologies and advanced traditional techniques with available local materials is essential. The application of agro-waste for sustainable building materials provides a solution, which offers a reduction in the use of the natural resource as well as energy. A large demand has been placed by the building material industries, especially in the last decade, owing to the increasing population, which is causing a chronic shortage of building materials. However, to meet the increasing housing demand, there is an exponential need for the production of building materials, like bricks, cement, aggregates, wood, cladding and partitioning materials from agricultural waste material. They are using Palm Kernel Shell as Lightweight Aggregate for Concrete and Ceramics. Thus, countless agricultural waste products can be used as raw materials for the production of building materials.

4.4. India

4.4.1. Preparation of Handmade Paper from Jute Waste

The handmade paper/paper board is made from low grade jute fibre and can be suitably blended with other lignocellulosic fibres by adopting an inexpensive pulping process with minimum use of cooking chemicals like caustic soda, sodium carbonate, lime etc.

4.4.2. Utilization of Corn Cob Powder for Kulhad Making

Traditionally mud cups (kulhad) are prepared using red mud. Continuous depletion of source has affected the availability of this mud and consequently there is need to develop alternatives to fully or partially replace red soil in Kulhad making. Corn cobs, otherwise a waste product, are utilized for making mud cup to convert this waste into value added product.

4.4.3. Biochar from Agricultural Waste Material

Agricultural biomass can be converted into biochar within two hours with a conversion efficiency of 25-35% depending on the type of biomass by using modified portable metallic kiln to improve soil fertility and crop yield and Increase fertilizer use efficiency.

4.4.4. Soil less Planting Media using Sugar Industry Residue

The press mud, a residual product in Sugar Industry that is available abundantly at the rate of 2 percent of the cane crushed, has physical properties similar to soil and provides good anchorage to plant roots. The press mud once composted provides essential nutrients to plants. Hence a soil less planting media is formulated using composted and powdered press mud.

5. CONCLUSION

Agricultural wastes are residues from the growing and processing of raw agricultural products are non-product outputs of production and processing and may contain material that can benefit man. These residues are generated from a number of agricultural activities and they include cultivation, livestock production and aquaculture. These wastes when managed properly through the application of the knowledge of agricultural waste management systems. It is important to not from the findings so far that proper waste collection, storage, treatment, transfer, and utilization is a panacea to a healthy environment. Proper waste utilization will assist in developing our agricultural sector and provide viable biofuel resource for many.

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Treatment of cancer by inhibiting zinc containing metalloenzyme

Project Work

Submitted for partial fullfillment of the B.Sc Degree in Chemistry

By

Subho Ghosh

Under the supervision of Dr. Ranjan Patra

Subho Ghosh

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Date:-26/12/2021

Place:-Rahara

Treatment of cancer by inhibiting zinc containing metalloenzyme

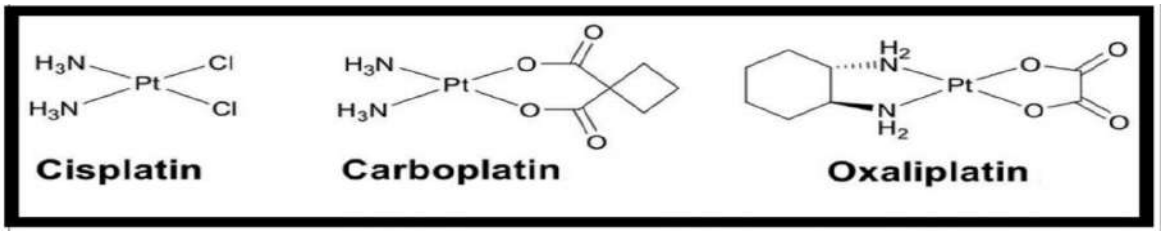
Abstract:

Metal containing enzyme (i.e Metalloenzymes) are enzyme proteins containing metal ions (metal cofactors), which are directly bound to the protein or to enzyme-bound nonprotein components (prosthetic groups).Metalloenzymes are metalloproteins that perform a catalytic function. Metalloenzyme are a part of all enzymes and are very important in a wide range of biological process such as DNA modification , protein Romeostasis ,antibiotic resistance and many others.

This review article is mainly focused on zinc containing metalloenzyme inhibition of metal based anti Cancer agents, different metal binding fragments and their chelating property and through FBDD an effort is also performed to connect between Bioinorganic and medicinal chemistry.

Introduction :

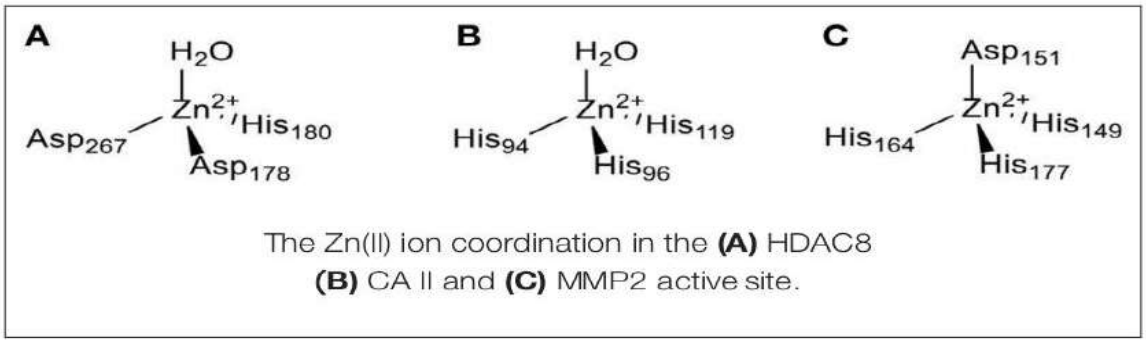
After the discovery of platinum-based drugs developed the metal-based anticancer agents. The example of platinum based drags such as cis platin, carboplatin and oxaliplatin which are used in the treatment of cancers .DNA is consider to be the primary target of platinum based drugs .Though, Anticancer drugs involve in the DNA binding mechanism may damage the normal cells and cause the serious side effects .zinc complexes generally exert lower toxicity in comparison to other metal-based drugs and many zinc derivatives have been proposed as antitumor agents.



Fragments based drug discovery (FDBB) is very important drug discovery approach and also fitted for metalloenzyme inhibitor development . For metalloenzyme inhibition , a metal dependent

active site is highly required . Till now , survey of many molecular fragments for binding the metal active sites of metalloenzyme is still undiscovered.

Many Metalloenzymes have been proved to important targets for cancer therapy.some metalloenzymes contain a zinc(II) ion at the active site of the enzyme .Mainly three zinc-containing metalloenzymes expressed in tumors, such as histone deacetylases (HDACs), carbonic anhydrases (CAs), and matrix metalloproteinases (MMPs).HDACs are highly expressed in lung cancer, colon cancer, prostate cancer, and breast cancer . CAs have been reported to be overexpressed in lung cancer, colorectal cancer, and gastrointestinal stromal tumors.MMPs expression has been found in cervical cancer. These three zinc- containing metalloenzymes are all involved in the genesis and development of cancer .The catalytic active centers of HDAC8, CA II and MMP2 are shown in below the picture.



The Zn(II) ion coordination in the **(A)** HDAC8 **(B)** CA II and **(C)** MMP2 active site.

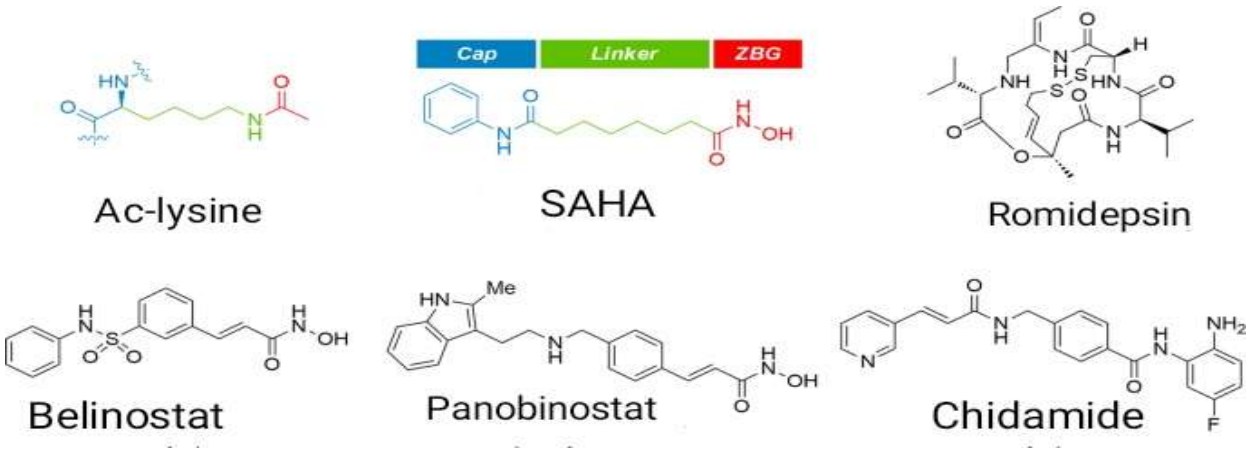
SUMMARY OF THE PROJECT WORK :

Some zinc-containing metalloenzymes are histone deacetylases (HDACs), matrix metalloproteinases (MMPs) and carbonic anhydrases (CAs).

1.Histone deacetylases :

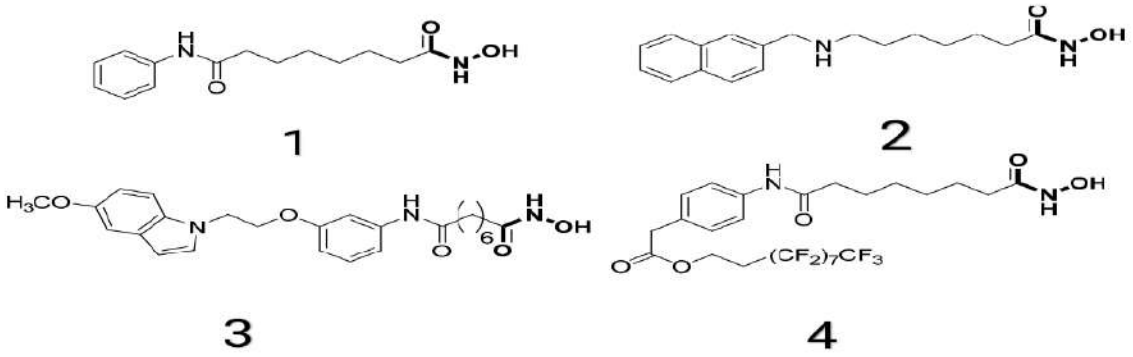
Total 18 number of HDACs are present which are divided into four categories.Class I consists of HDAC1, 2 and 8. Class IIA contains HDAC4, 5, 7 and 9. Class IIB contains HDAC6 and 10. class III is called as surtuins1-7, while Class IV has only one member,HDAC11. All of the histone deacetylases are metal-dependent except member of Class III. HDACs are highly expressed in

breast cancer and lung cancer etc. HDACs are considered therapeutic targets for a many type of diseases such as metabolic disorders , cancer, autoimmune disease, inflammation etc. Generally classify HDACs into hydroxamic and non-hydroxamic. HDACs have become one of the most important targets for cancer treatment. The first clinically approved HDAC inhibitor used for the treatment of cutaneous T-cell lymphoma. Many HDACs including vorinostat (suberoylanilide hydroxamic acid, SAHA) , valproic acid(VPA), romidepsin ,and panobinastat have been approved by FDA for the treatment of cancer.



Different HDAC inhibitors having Zn^{2+} chelating group

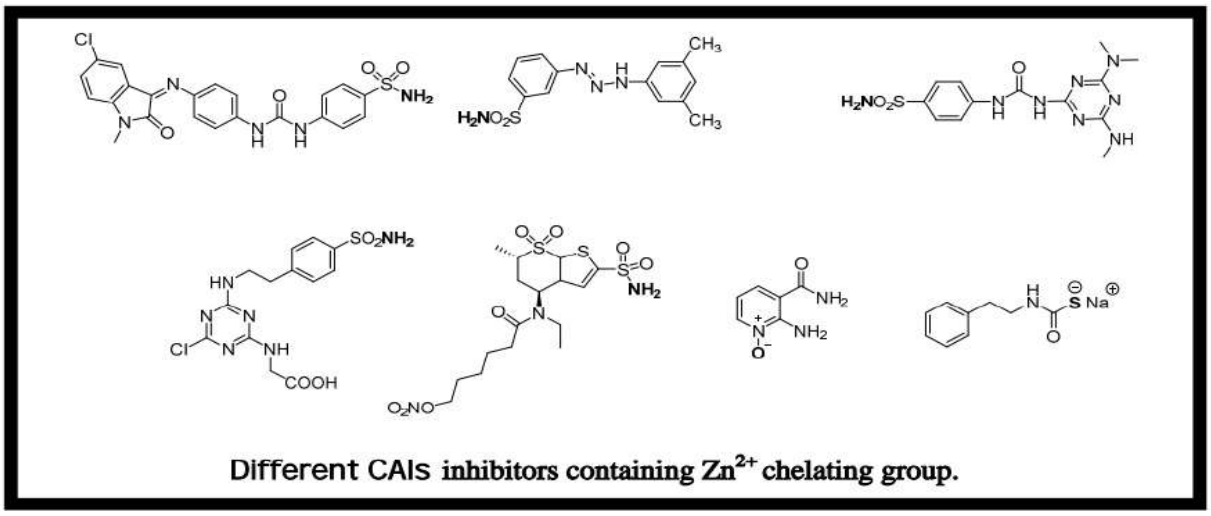
SAHA is the first FDA approved HDACi to enter the clinic. Compounds 2, 3 and 4 adopt the six carbon aliphatic chain of SAHA. Compounds 2 and 3 are both Class I HDAC inhibitors. Compound 2 displays potent cytotoxic activity against colorectal adenocarcinoma HT-29 and breast adenocarcinoma MCF-7 , while 4 shows toxicity toward ovarian cancer A2780 cells.



HDAC inhibitors containing Zn^{2+} chelating group.

2.Carbonic anhydrases :

Carbonic anhydrase (CA) was the first discovered Zn^{2+} dependent metalloenzyme which catalyze the reversible hydration of Carbon dioxide to bicarbonate . Carbonic anhydrase inhibitors (CAIs) are used to treat cancers. Many CAs isoforms play key roles in physiologic processes, including acid-base equilibrium. Carbonic anhydrases (CAs) play a key role in the regulation of acid-base equilibrium in tumor cells. Carbonic anhydrases (CAs) protect the tumor cells by maintaining intracellular pH near physiological levels.The sulfonamide group (R-SO2NH2) is one of the classical Zinc binding groups(ZBG) of Carbonic anhydrases inhibitors (CAis).The sulfonamide group (RSO2NH2) binds to the Zn(II) ion at the active site of CAs by deprotonation. Most clinically used Carbonic anhydrases (CAis) is acetazolamide(AAZ) which contain sulfonamide group (R-SO2NH2) .

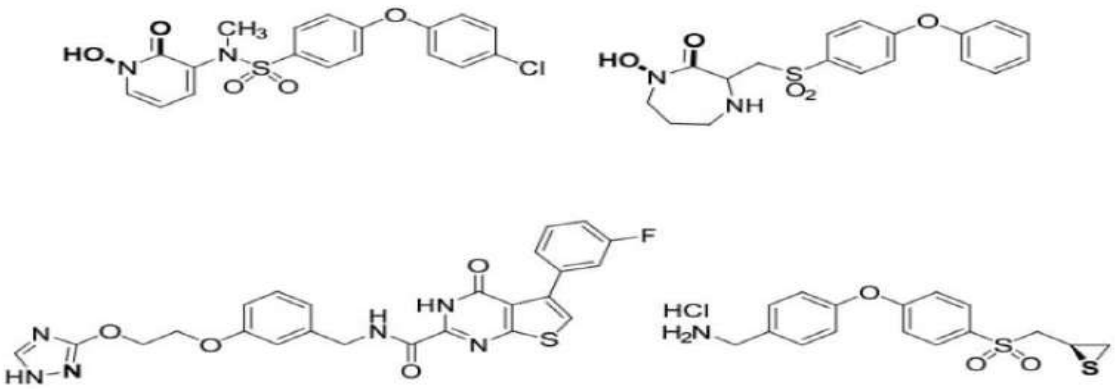


Different CAIs inhibitors containing Zn^{2+} chelating group.

3. Matrix metalloproteinases :

Matrix metalloproteinases (MMPs) are a family of zinc-dependent endopeptidases that are involved in the cleavage of extracellular matrix and cell membrane components such as collagen proteoglycan, elastin, fibronectin, gelatin, laminin, etc. Under normal physiological conditions MMPs are involved in the maintenance of extracellular matrix homeostasis, tissue remodeling,

wound healing, apoptosis ,angiogenesis and other important physiological processes. The abnormal expression of MMPs has been found in many diseases, including tumor invasion .Hydroxamic acid has been used as a Zinc binding group(ZBG) in MMPis .Synthetic inhibitors generally contain a chelating group that binds the catalytic zinc atom at the MMP active site tightly.



Different Matrix metalloproteinase inhibitors containing Zn^{2+} chelating group.

Conclusion :

Platinum-based drugs, such as cisplatin , carboplatin and oxaliplatin are being used in treatment of cancers and DNA is considered to be the primary target of platinum based drugs . Anticancer drugs involved in the DNA binding mechanism may damage normal cells and cause serious side effects .Many metalloenzymes have been proven to be important targets for cancer therapy.Zinc containing metalloenzyme are significantly more active than cisplatin . Treatment of cancer is always a topic of interest to many researchers. As application of Bioinorganic chemistry in medicinal field comparatively new concept, researchers are trying to implement the applications in cancer therapy to serve the need of people.

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HYDROGEN PRODUCTION FROM THE CATALYTIC DECOMPOSITION OF FORMIC ACID OVER IRIDIUM-PALLADIUM NANOPARTICLES

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

Subhradeb Chakraborty

Under the supervision of Dr. *Kaustab Mandal*

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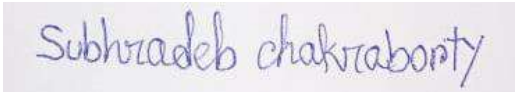

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ABSTRACT :

The present study investigates a process for the selective production of hydrogen from the catalytic decomposition of formic acid in the presence of iridium and iridium–palladium nanoparticles under various conditions. It was found that a loading of 1 wt.% of 2% palladium in the presence of 1% iridium over activated charcoal led to a 43% conversion of formic acid to hydrogen at room temperature after 4 h. Increasing the temperature to 60 ◦C led to further decomposition and an improvement in conversion yield to 63%. Dilution of formic acid from 0.5 to 0.2 M improved the decomposition, reaching conversion to 81%. The reported process could potentially be used in commercial applications.

INTRODUCTION :

Fossil fuels are non-renewable energy sources, as these sources will not last forever, and their supply is declining. The expected growth in global energy consumption must be accompanied by the introduction of carbon-neutral energy generation and carrier systems to reduce modern societies' environmental footprints and overcome the limitations of fossil fuel resources. Renewable biofuels, electricity from nuclear power stations, and solar and wind technology are the most popular contenders for such developments. New materials that can facilitate the technological advancements towards transition to a hydrogen economy are of paramount interest. Chemical hydrogen storage materials are of recent interest among material scientists due to their high hydrogen capacities, which is one of the key requirement for developing a hydrogen-based society [1]. In this regard, the liquid hydrogen carrier formic acid (FA) has become an attractive choice. Renewable and sustainable energy sources are targets for commercial uses in the near future. Several sustainable energy sources, such as solar and nuclear energy and lithium-ion batteries, have been extensively explored. Recently, the use of hydrogen as an important source of energy for future applications has gained attention. Hydrogen is an environmentally friendly energy source with an energy density of 120 kJ g−1 and water as the only by-product of its combustion [2,3].

Hydrogen can be obtained cleanly from the decomposition of formic acid (FA). FA is a commodity chemical, found in nature in the venom of ants,

and can be obtained as a by-product from bio-refinery processes. Implementing a new strategy that involves the low-temperature synthesis of FA from biomass could enable the use of FA in the industrial-scale production of fuel [4]. However, various limitations hinder the use of hydrogen as an energy source, such as the safe storage and limited capacity of hydrogen and its transportation as an energy carrier [5]. Therefore, significant efforts have been made to overcome such limitations. The most common approaches for hydrogen storage involve the use of sorbent materials [6], metals, and chemical hydrides [7].

Homogeneous catalysts are not a viable option for FA decomposition, because separting them from the reaction mixture is difficult and requires additive(s), ligands, and organic solvents, which are undesirable for industrial applications. Therefore, heterogeneous catalysts are preferable. The use of commercial palladium (Pd) over activated carbon (C; 5% by weight) as a catalyst led to an excellent selectivity toward hydrogen production [8]. Metal–organic frameworks have been used for gas sorption and storage, owing to their high surface area [9]. The use of gold–palladium (Au–Pd) and silver–palladium (Ag–Pd) nanoparticles drives the reaction selectivity toward the desired pathway at a lower temperature [10]. Furthermore, a Co Au Pd nanoalloy supported on carbon has been used as a selective catalyst in the decomposition of FA to produce hydrogen, with a high conversion rate (91%) at room temperature [11]. Such a catalyst is cheap, easy to prepare, and stable, with no CO produced. Other catalysts such as

Ag–Pd core–shells, Ag–Pd bimetallic NPs, platinum–copper (Pt–Cu) single-atom alloys have been used successfully in the selective decomposition of FA to hydrogen at mild temperatures [12,13].

In this paper, we report the successful use of iridium (Ir) and Ir–Pd nanoparticles as catalysts in the decomposition of FA using impregnation and sol-immobilization techniques under various reaction conditions.

RESULTS & DISCUSSION :

(a)Catalyst Characterization : An Ir:Pd/C 1:2 (1 wt.%) XRD diffraction pattern was observed, as shown in Figure 1. The samples' diffraction peaks at 22.2◦ for the prepared catalyst revealed an active carbon structure. The (111), (200), and (220) planes of the face-centered cubic architecture of Pd were assigned to Pd peaks at 40.1◦ , 45.6◦ , and 69.9◦ , respectively. Moreover, the diffraction peaks at 2θ of 41.7◦ , 47.1◦ , and 70.1◦ could be attributed to the (111), (200), and (220) planes of face-centered cubic Ir, respectively.

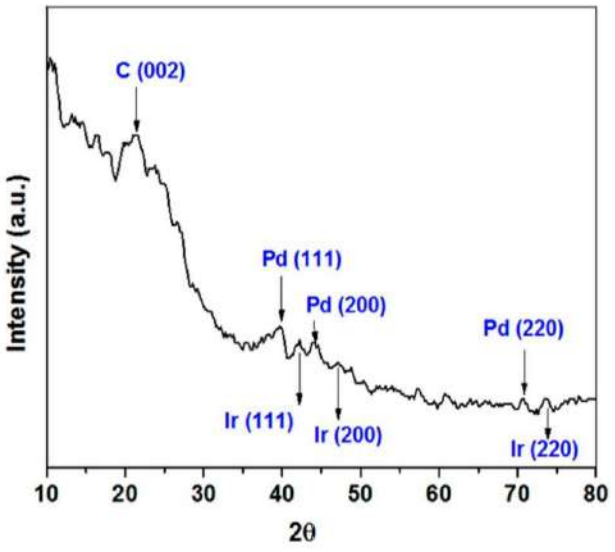

Figure 1 X-ray diffraction patterns of 1% Ir: 2% Pd/C sample.

The nature of the surface oxidation state for the 1% Ir:2% Pd/C catalyst was investigated using XPS; the XPS survey spectrum of Ir:Pd/C 1:2 (1 wt.%) is displayed in Figure 2a, while the Pd 3d spectrum and the Ir 4f spectrum of the same catalyst are shown in Figure 2b,c, respectively. The XPS spectrum of Pd 3d is displayed in Figure 3b. Two major doublets were found in the Pd 3d spectrum, suggesting two separate Pd oxidation states: Pd(II) and Pd(0). Furthermore, because Ir metal is readily oxidized to Ir-oxide (IV) in ambient conditions, the XPS spectrum of Ir 4f can be deconvoluted by two sets of curves based on the existence of the oxidized Ir(IV) and metallic Ir. For the Ir:Pd/C (2:1) catalyst, the peaks at 61.1 and 62.9 eV are attributed to the Ir and the peaks at 53.2 and 58.1 eV are attributed to the Ir(IV) oxidized form.

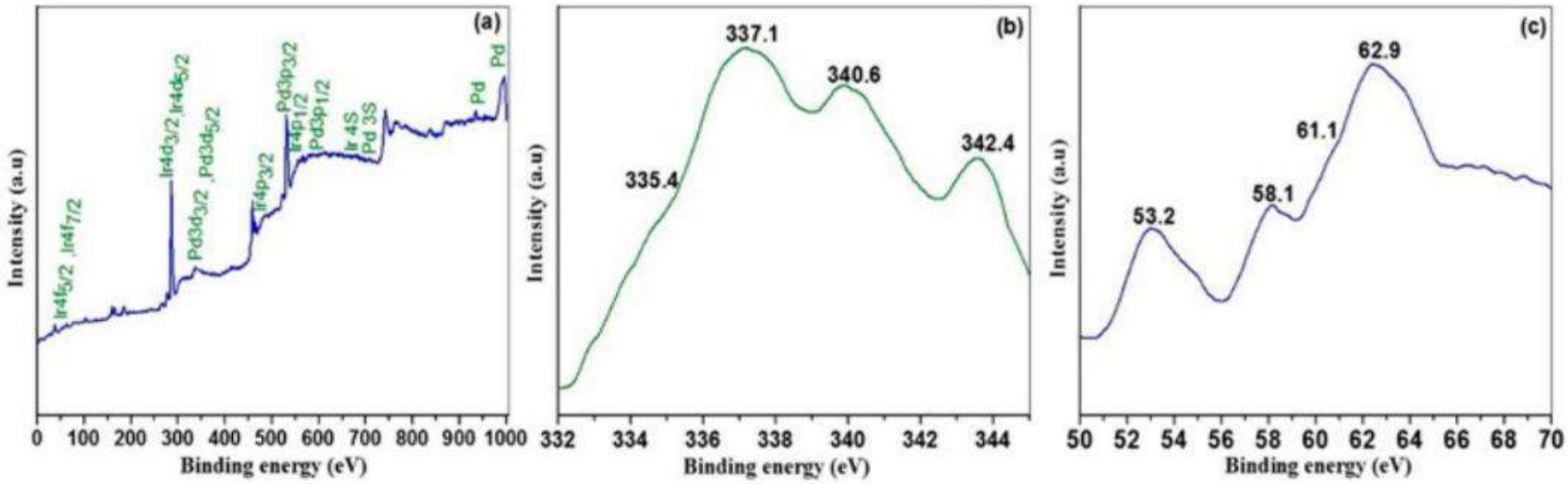

Figure 2. XPS analysis of (**a**) 1% Ir:2% Pd/C, XPS survey spectrum; (**b**) Pd 3d spectrum; and (**c**) Ir 4f spectrum of the same catalyst.

(b) Catalyst Activity in FA Decomposition :

Two catalysts were prepared with Ir:Pd in a 1:1 ratio over activated charcoal using impregnation and sol-immobilization methods. Both catalysts were used to decompose formic acid at 25°C, and the reaction mixture was stirred at a speed of 700 rpm for 4 h. Carbon dioxide and hydrogen were the only products detected in the gas phase, with no evident carbon monoxide formation. The results show that the catalyst, which was prepared with the sol-immobilization technique, decomposed the FA more efficiently, by 16.42%, whereas the catalyst prepared with the impregnation method decomposed FA by only 6.6%. A similar observation was previously published in the literature [14]. Therefore, we used the sol-immobilization method for all further experiments. Several Ir and Ir–Pd catalysts over activated charcoal were prepared and tested for the decomposition reaction of FA in the liquid phase. The catalyst was added to FA with a substrate:metal molar ratio of 2000:1 at 25 °C, and the reaction mixture was stirred at a speed of 700 rpm for 4 h. Carbon dioxide and hydrogen were the only products detected in the gas phase, with no evident formation of carbon monoxide. It can be seen from the graph in Figure 3 that Pd/C showed a higher decomposition activity than Ir/C; the results were 36% and 23%, respectively, after 240 min. In bimetallic catalysts, better activity was observed. For example, Ir:Pd/C 1:2 (1 wt.%) exhibited the highest activity, with approximately 43% of the FA being converted into H2 and CO2.

No further improvement in conversion was observed when the amount of Ir in the bimetallic catalyst was increased. Pd was present at 335.5 eV (Pd0) and 337.1 eV (Pd2+), which was different from that of the monometallic catalyst, where both Pd–Cl and PdO were observed. Notably, the Pd(0) binding energy was somewhat higher than what was expected for metallic Pd particles, which may be attributable to Pd2+ species formed by a charge transfer with Cl-1 that remained on the surface or the particle size-dependent screening effects of the Pd core–hole that resulted in higher binding energies for smaller particles [15]. Therefore, the Ir:Pd/C 1:2 catalyst was used in further investigations of FA decomposition.

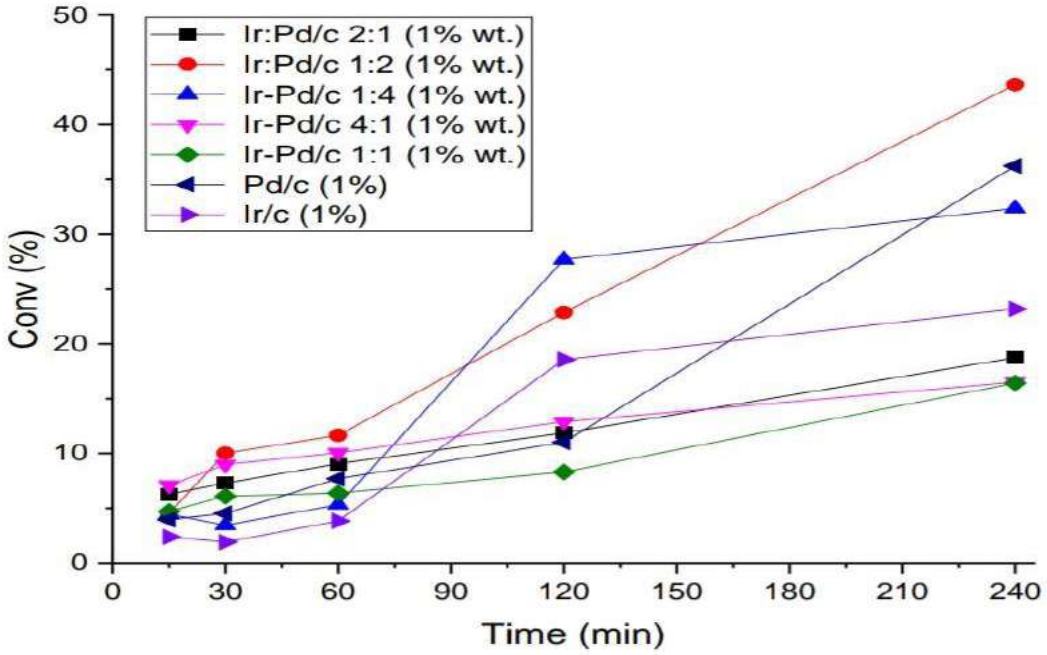

Figure 3 Catalytic decomposition of FA. Reaction conditions: FA (0.5 M), catalyst (substrate:metal molar ratio = 2000:1), 25 °C, 700 rpm, and 240 min.

The effect of temperature on FA decomposition was investigated using the Ir:Pd/C 1:2(1 wt.%) catalyst. The temperature was varied from 25 to 80 °C for 4 h. The results are presented in Figure 4. When the reaction was conducted at 25 °C, the conversion rate of FA to H2 and CO2 was only 43.6%. Increasing the temperature further to 40 °C led to an improvement in FA decomposition (48.1%). The decomposition of FA was improved further when the temperature was 50 °C, reaching 63.3% after 4 h.

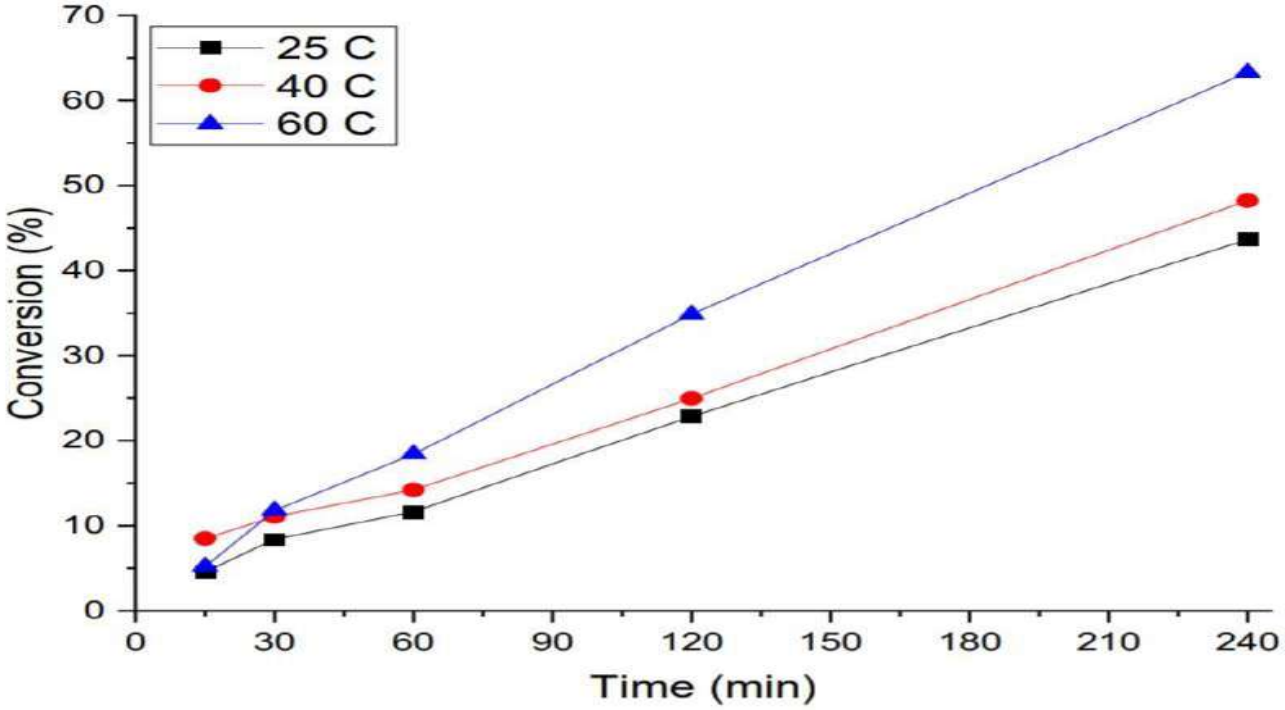

Figure 4. Effect of temperature on FA decomposition over 1%Ir:2%Pd/C. Reaction conditions: FA (0.5 M), catalyst (substrate:metal molar ratio = 2000:1), 700 rpm, and 240 min.

The activation energy (ΔG), calculated from the slope of the Arrhenius plot, was found to be 4.2 KJ/mol. The TOF and ΔG results, along with the reported values obtained for the decomposition of FA over other catalysts, are shown in Table 1.

Table 1. Catalytic activities of different types of catalysts for the decomposition of formic acid.

Catalyst (wt.%)	T (°C)	FA (M)	TOF (h^{-1})		ΔG (KJ/mol)	Ref
			Initial	2 h		
2%Ir:1%Pd/C	25	0.50	–	4.12	4.2	This work
Pd_{IMP}/CNF	30	0.50	563.2	–	27.5	[16]
Pd_{SI}/CNF	30	0.50	979.1	–	26.2	17
Pd_{SI}/AC	30	0.50	240.5	–	–	18
Pd/C	21	1.33	18	15 [a]	53.7	[19]
Pd/C	30	1.33	48	28 [a]	–	[20]
Pd/C (citric acid)	25	–	–	64 [b]	–	[21]
Pd/C	30	1:9 [c]	–	228.3	–	[22]
$Au_{41}Pd_{59}$/C	50	1.0	230		28 ± 2	[10]
Ag@Pd (1:1)	35	–	–	156 [d]	30	[23]
Ag@Pd (1:1)	50	–	–	252 [d]	–	[24]
Ag/Pd alloy (1:1)	20	–	–	144 [d]	–	[25]
$Ag_{42}Pd_{58}$	50	1.0	382	–	22 ± 1	[26]
Pd-MnOx/SiO_2-NH_2	20	0.265	140	–	61.9	[27]
Pd-MnOx/SiO_2-NH_2	50	0.265	1300	–	–	[28]
$Ag_{0.1}Pd_{0.9}$/rGO	25	–	105	–	–	[29]

[a] TOF was calculated after 50 min. [b] TOF was calculated after 160 min. [c] The ratio between FA and sodium formate was 1:90. [d] TOF was calculated based on the surface metal sites.

The catalyst activity after further reuses was studied at 25 ◦C and 700 rpm, with a concentration of 0.5 M formic acid (substrate:metal molar ratio = 2000:1) and a reaction time of 2 h. The reusability test was conducted by filtering the catalyst at room temperature and atmospheric pressure and using it in a fresh reaction under the same reaction conditions. showed some loss in their activity after the first use, as shown in Figure 5. The catalysts stabilized after the second run. The loss of their activity might be due to increased particle size or agglomeration, the formation of metal species, or the adsorption of formate species [30] For several potential reasons, such as the loss of the active species through reduction, Pd particle sintering, or the active Pd site being covered by coke or adsorbed reactants / products, are reported in the literature[31].

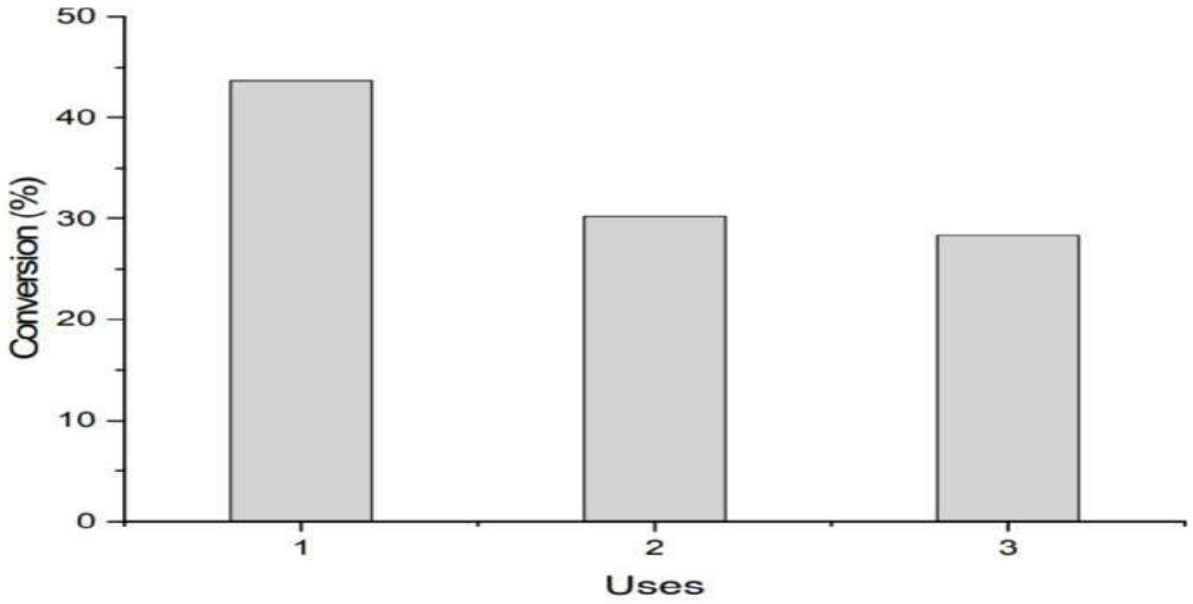

Figure 5. Reusability of 1%Ir:2%Pd/C after three reactions. Reaction conditions: 31 mg of catalyst, 25 °C, 0.5 M FA, 700 rpm, 2 h reaction time.

CONCLUSIONS :

The decomposition of formic acid was carried out selectively to produce hydrogen and carbon dioxide using 2% Ir:1% Pd (by weight) loaded over activated charcoal at 25 °C for 4 h. The Ir–Pd bimetallic catalysts were stable and showed powerful interactions and high dispersions on the charcoal support. The selective production of hydrogen from the complete catalytic decomposition of FA could be used as an efficient and valuable process for the production of clean fuel.

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A REVIEW

ON

EFFECTIVENESS OF COPPER AND COPPER BASED MATERIALS ON KILLING OF COVID-19

Project Work Submitted for Partial Fulfillment of the B.Sc. (Honours) Degree in Chemistry

BY

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Registration Number: A01-1112-112-017-2019 of 2019-2020

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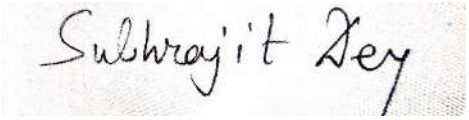
Finally, my deepest admiration goes to my parents for their all-out support throughout my life.

….  ……..

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Date: 15/01/2022

Place: Tehatta, Nadia

EFFECTIVENESS OF COPPER AND COPPER BASED MATERIALS ON KILLING OF COVID-19

Abstract

Copper (Cu) and its alloys are prospective materials in fighting covid-19 viral and several microbial pandemics, due to excellent antimicrobial property. Several studies conducted on copper and its alloys have proven that copper-based alloys possess excellent potential to control the spread of infectious disease. Moreover, recent studies indicate that these alloys can effectively inactivate covid-19 virus. In this project antimicrobial property of copper and copper-based materials are discussed along with their effectiveness of covid-19 with mechanism. This study shows how copper, nanomaterials of copper and copper-coating surfaces affect on microbial growth. Overall, how copper-based materials can be propitiously used as a part of preventive and therapeutic strategies in the fight against covid-19 virus**.**

Introduction

This project especially shows how covid-19 and other viruses affects the health. Covid-19 is a type of coronavirus. There are many types of viruses and some cause disease. A coronavirus identified in 2019, SARS-CoV-2, has caused a pandemic respiratory illness, called covid-19.

Researchers know that coronavirus is spread through droplets and virus particles released into the air when an infected person breathes, talks, coughs or sneezes. Larger droplets may fall to the ground or surfaces in a few seconds, but tiny particles can linger in the air and accumulate in indoor places, especially where many people gathered and there is poor ventilation. This is why mask wearing, hand sanitizing and physical distancing are essential to prevent covid-19. The 1st case of covid-19 was reported in Dec 1,2019 and the cause was a then-new coronavirus later named SARS-CoV-2.

In this portion we will discuss how copper contact affects covid-19 virus along with other viruses, how microbial growth is affected by copper and so on. We will compare other material with copper and then will draw a conclusion.

History of copper usage on medicine

Copper has many special properties and has a great effect on our immune system. One of them be antiviral property. Any virus or microbes can not live in copper surface more than 4hrs. Copper had a great usage in ancient civilization. It would be used in many medical purposes. In ancient Egypt copper and its derivatives were used for water sterilization. In Roman civilization it was used to cure headache, intestinal worms, infections in ear and for general hygiene. Copper-based materials were also used for the treatment of ulceration in Greece. Copper dust along with honey had a great application in antiseptic purposes. In ancient India copper dust was a common material to use as medicinal element.

Use of “Tamra Patra” is also described in Chakra Samhita. In 19th and 20th century for the treatment of many diseases like chronic adenitis, scrofulosis, syphilis, impetigo, lupus, cholera, tubercular infections, eczema and facial neuralgia etc. copper was used. Before 1932, when antibiotics were prepared, it had been used as antimicrobial agent. Researchers showed that in the treatment of anaemia copper is more effective than iron.

Effect of copper deficiency on health

cardiovascular disease and osteoporosis. Copper has a great effect in our digestion system Copper is an essential nutrient for the body. Together with iron it enables the body to form RBC. It maintains healthy bones, blood vessels, nerves, and immune function and it contributes to iron absorption. Sufficient copper (about 2.6mg/day) may help prevent.

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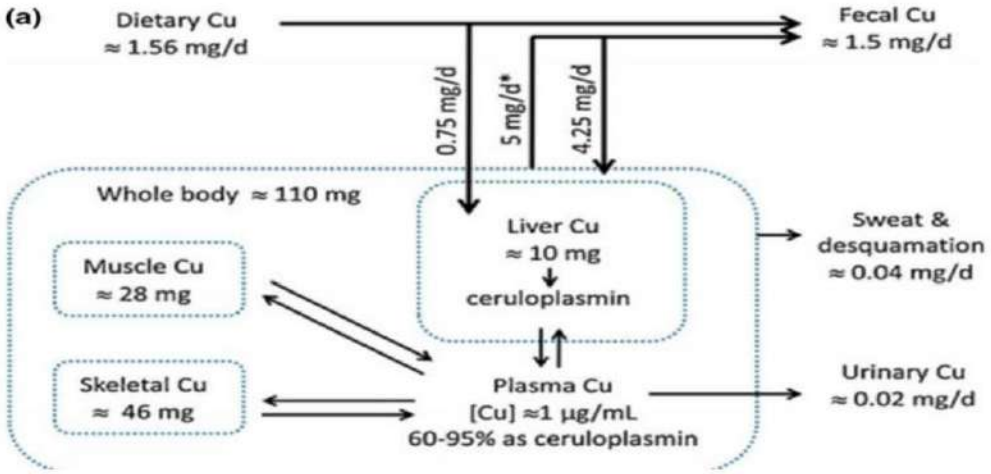

Fig-1

a)copper absorption by various organs

Due to deficiency of copper deficiency different types of diseases like cardiovascular, pulmonary neuronal, skeletal, immunological and behavioural function in offspring during infancy and beyond may appear. Copper deficiency may lead to parasitic infections affecting T-lymphocytes, monocytes, neutrophil and T-cell functions. Thus cell-mediated immunity gets affected. Functions of B-cell, T-helper cell and natural killer cells (phagocytes or macrophages) are inhibited. Moreover, it affects the generation of pathogen specific antibodies.

Antiviral mechanism of copper

Copper's toxic property kills the pathogens and resist the microbial attack. It has ability to generate ROS (reactive oxygen species) by which it can oxidize the cell of the microbes. Copper ion binding and cross linking between genome strands can damage the viral genomic DNA. DNA is a potential target for cytostatic drugs. Cu2+ binds to DNA (Fenton type reaction) and generates ROS which leads to the degradation of DNA. Copper can also destroy the microbes by degrading their genomic and plasmid DNA.

Any microbe present on copper surface cannot live much time. Presence of copper ions kill the virus or bacteria. This phenomenon is called "Contact Killing".

Five enveloped or non-enveloped, single or double stranded DNA or RNA viruses are inactivated in presence of Cu(II). Presence of peroxide catalyzes this process. Compared to Fe(II), Cu(II)-peroxide is more effective antimicrobial agent against herpes, T7, Φ×174, Φ 6 and Junin simplex viruses. Copper surface is more antimicrobial than stainless steel surface. Copper shows a significant decrease of 83% microbes compared to other metals.

A comparison of antiviral property between copper and stainless steel

TYPE OF SURFACE	TIME PERIOD	MICROBES PRESENT
COPPER SURFACE	After 6 hours After 24 hours	500 -
STAINLESS STEEL SURFACE	After 6 hours After 24 hours	- 500000

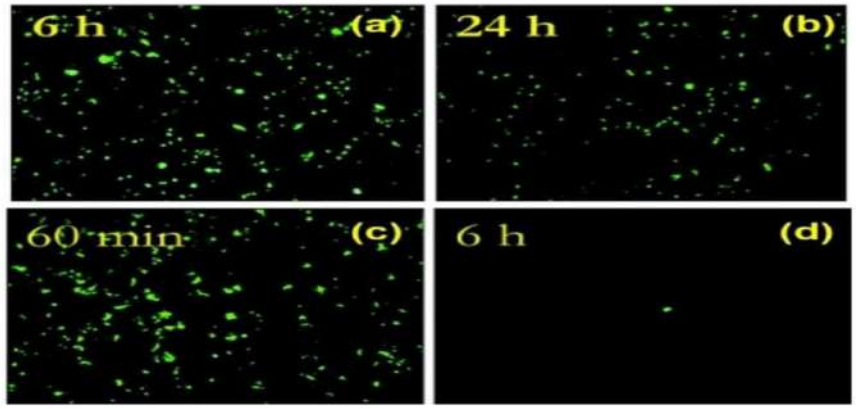

Fig-2

((a),(b) Influenja virus present on stainless steel surface after 6 and 24hrs respectively. (c),(d) Influenja virus present on copper surface after 6 and 24hrs respectively)

The viral genomes were disrupted by copper exposure, and the morphology was irreversibly changed, inducing the disintegration of envelop and dispersal of surface spikes. Inactivation triggered by Cu(I) and Cu(II) aided by ROS generation on alloy surface leading to faster inactivation as compared to non-enveloped viruses. In 'Contact Killing' mechanism at first copper enters into the microbial cell and destroy the DNA restricting their metabolism, respiration and reproduction. Again large amount of copper damage the cell-membrane of bacteria cells inducing the loss of cytoplasm. Further generation of ROS destroys the cells.

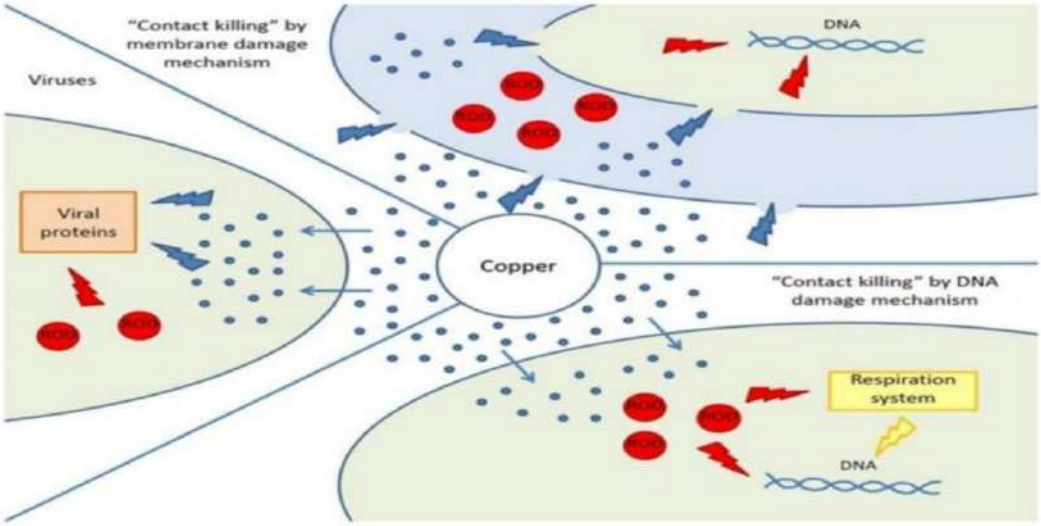

Fig-3

(Contact killing mechanism)

Effectiveness of copper on covid-19 in comparison with other material

In comparison with other materials, brass alloy with more than 70% copper, exhibit superior virucidal action on HuCoV-229E. there was no trace of viruses on the surface within a shorter time duration of 60 min where on the surface of stainless steel, plastic, PVC, glass and ceramics, there were viruses present even after 5 days. Virucidal effect is proportional to the copper content of an alloy. On the surface of stainless steel and plastics where SARS-CoV1 and SARS-CoV-2 were present even after 72hrs, copper surface were clear from them only after 8hrs and 2hrs respectively.

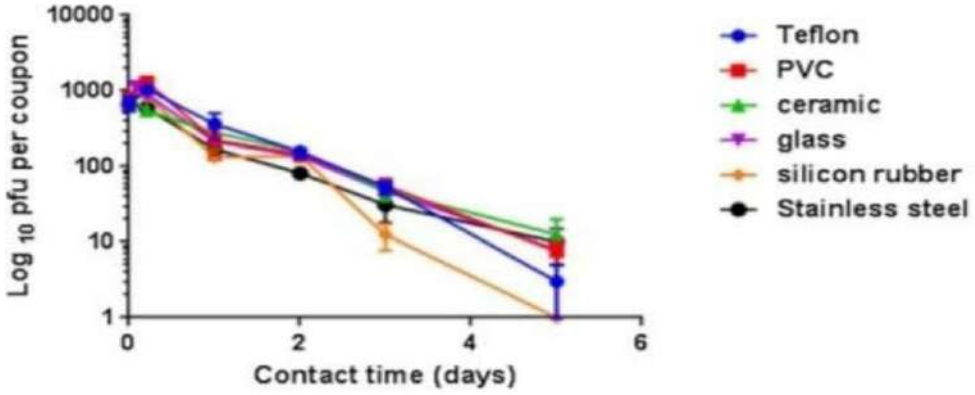

Fig-4

a comparison on virucidal action of different materials

Doctors and medical workers always come in contact with viruses. The surgeons and their surgery equipment also have a great chance to come in contact to the viruses. So, to disinfect or sanitize the equipment copper solution is very effective to shield the viral contamination. Copper, due to its rapid

inactivation, viral RNA destruction and structural damage, may be used in control of respiratory virus transmission such as MERS and SARS. Also used in highly touchable surfaces.

Copper based materials in fighting covid-19

Copper-based materials are daily used as surface disinfectant. Their antiseptic and antifungal effect make them special leading to the production of drugs.

COPPER-BASED ALLOYS: Recent studies have proved that copper-based alloys have great properties like antiviral, antibacterial and they can be used as virucidal drugs.

Copper alloy affects herpes simplex, bronchitis, HIV-1, hepatitis-C, murine norovirus (MNV-1), poliovirus, 44-monkeypox, covid-19 by damaging biomolecules, RNA, DNA, genomes and protein shell.

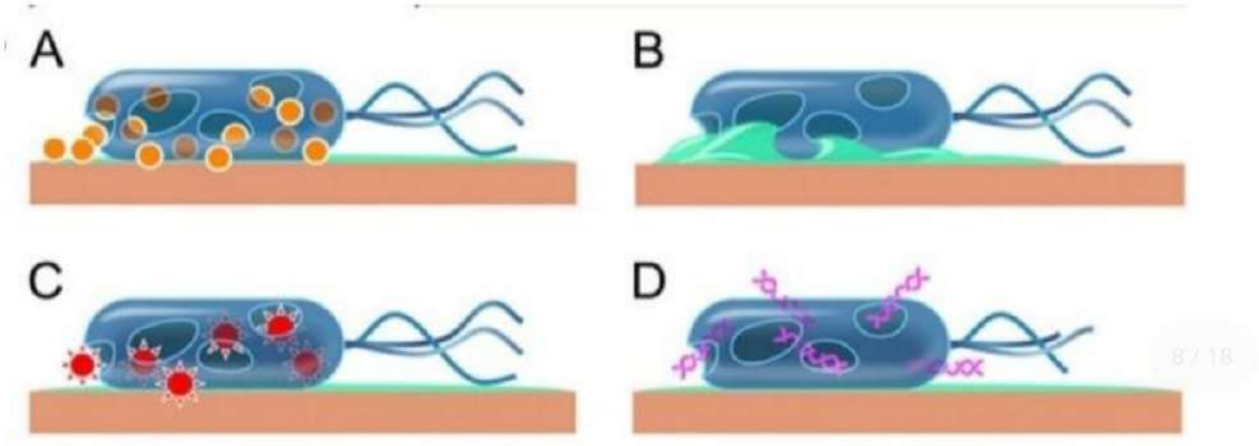

Fig-5

Illustration of contact killing mechanism on a copper surface (A) rupture of cell membrane, (B) loss of cytoplasmic content, (C) generation of other ROS by copper ions, (D) degradation of DNA

During experiment it is detected that less than 1.1log10 reduction in RNA copy number of HuNoV genome happened in stainless steel surface after a time period of 240min whereas, 2-3log10 reduction occurred only within 60min with 70% copper alloy.

Copper bearing stainless steel 316L-Cu SS was favourable as antibacterial substance preventing Implant Related Infection (IRI) both in vitro and in vivo. Copper alloy takes minutes or hours to inactivate viruses depending upon wheather the virus is gram-positive or gram-negative, enveloped or non-enveloped. It is also seen that in case of norovirus (MNV) pure copper metal took 30min to kill the surface-germs and copper alloy took 60min. This study is temperature dependent.

These values and data are obtained electronic microscope images. Copper-based material, calcined copper (Tamra Bhasma; Ayurveda) is effective on similar microbes. But Tamra Bhasma with and without Amrutikarana did not show any toxicity at low level but shows mild toxicity in liver, kidney, heart, thymus on rats. Copper glass ceramic powder destroys plasmid DNA and RNA. This powder reduce greater than 99.9% bacterial colony.

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NAME OF THE MICROBE	COPPER ALLOY NAME	MICROBES KILLED AFTER 12HRS	MICROBES KILLED AFTER 24HRS
E.coli	Ti-Cu	96.8%	99%
S . aureaus	Ti-Cu	80%	99%
Anaerobic Polyphyromonus gingivails	Ti-10 Cu {10% Cu}	-	75%
H1N1	CuFeCrCoNi	-	99.99%

Copper based nanoparticles(NPs)

Nanoparticles having diameter less than 100nm have medical properties and used in drug synthesis and therapeutics. The NPs are associated with wide surface area which assist in improving interaction with microbes, affects on a broad spectrum of microbes. Recent studies are improving to induce antimicrobial activity of NPs.

Metal NPs have potential to stop viral replication and propagation causing viral inactivation and virucidal effects by blocking cell-virus attachment and stop the entry of virus into the cells. Thus NPs can be used against many human pathogens like herpes, bronchitis, SARS CoV, poliovirus etc. NPs destroy the outer layer of covid-19 virus. Copper based NPs are used as biocidal in wounds dressing and socks. Broad spectrum activity on many enveloped and non-enveloped virus leads to use of copper as antiviral agents, which can induce cytotoxicity in microorganisms. NPs can degrade the capsid protein of norovirus. H1N1 and herpes like viruses are killed by oxides and iodides of NPs.

NPs are used as antifouling agents. CuI-NPs are used in mask, filters etc. Ayurveda describes many antiviral properties of several Ayurvedic Bhasma like Tamra Bhasma(Cu-NP), Rajata Bhasma(Ag-NP), Swarna Bhasma (Au-NP), Lauha Basma (Fe-NP) etc. NPs are used for drug production also. Bacterial colony may be destroyed more by increasing Cu concentration of CuO and CuI NPs. Cu has great affinity towards S and P and so it destroys viral DNA. They penetrate the cell membrane causing membrane damage, loss of cytoplasm and DNA degradation. Ag-Cu alloy prevent HIV replication and E. coli growth

Copper ions form complexes with biomolecules which causes protein degradation also. Cu-NPs have anti-parasitic and anti-cancer property as well.

Copper based coating technologies

Bulk component materials of copper may be replaced by Cu-based or Cu-coated surface. Cold-spray technique is used to deposit copper on surface like stainless steel surface which exhibit viricidal activity in a short duration of 7min. Through cold-spray technique making 0.7mm coating 96% covid-19 virus within 2hrs and 99.2% covid-19 virus within 4hrs may be removed.

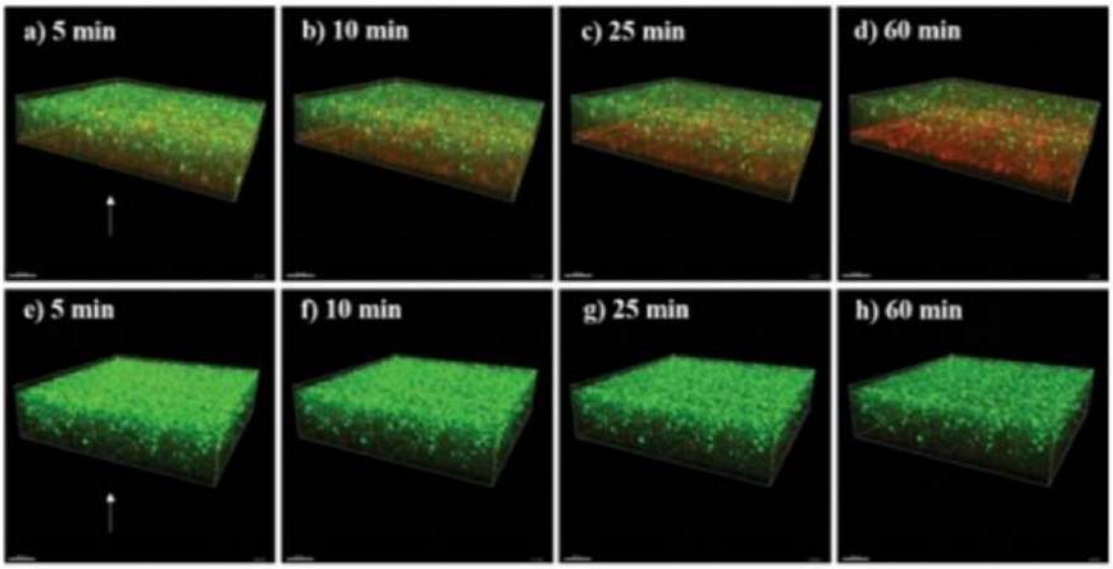

Fig-6

Increased bactericidal activity as evidenced by the presence of more dead cells (red colour, a–d) on copper–silver alloy coating compared to uncoated stainless steel surfaces with predominant live cells (green colour, e–h)

'Quick and fix' method and 'Thermal spray' method are also used to make copper coated surface. For antibacterial use copper coated plate may be used in daily use surfaces like door push-plate, chair arms, charting tables etc. Various microbes like Pseudomonus, E.coli, Staphylococcus etc. are killed on copper surface. Improved bacterial resistant has been explained to be arising from-

a) bacterial cell oxidation due to galvanic coupling induced redox reaction

b) copper ion release and

c) localized rise in pH.

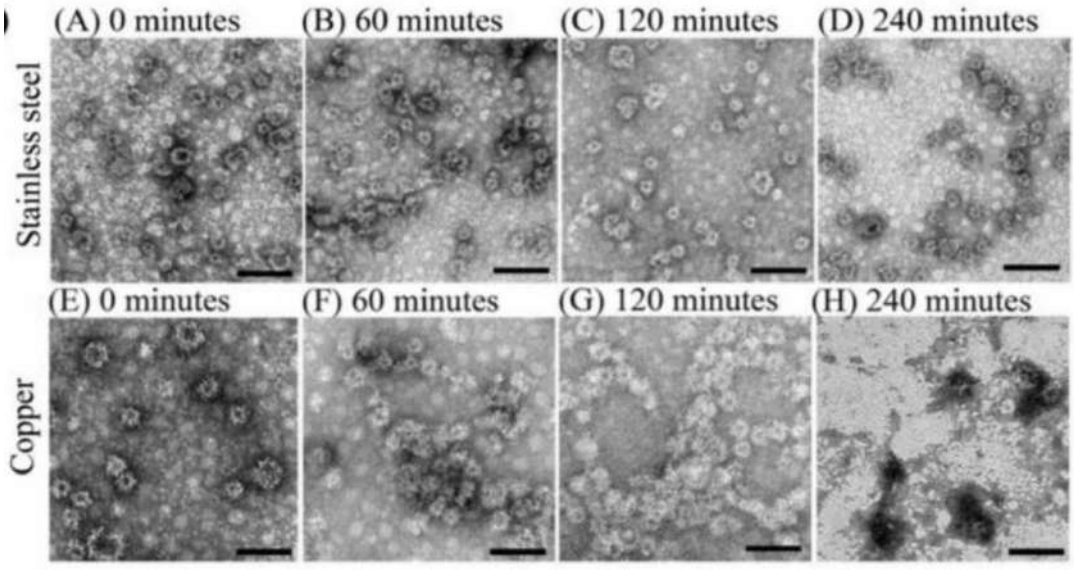

Fig:6

(Virucidal properties of copper and stainless steel)

The development surfaces show biofilm eradication of gram positive bacteria within short time as compared to slow removal of gram negative bacteria.

For controlling the spread of covid-19 cyta-coat (bio-compatible antibacterial covering) in face mask. Fluidic coating compounds can also be used as antiviral coating material made of nanomaterials with a significant high heat impact. They can form localized hot-spots under light stimulation and destroy viruses or inactivate the spike proteins

Fig:8 ;Application of copper

Limitations of copper usage

Inspite of its excellent antiviral properties, copper-based materials have some limitations which need to be taken into account for effective medical applications, copper is essential for humans and deficiency of copper affects health. Since, deficiency and excess of copper can have negative health effects, assessing copper specifications and upper safe limits for intake is difficult. Since copper is expensive and harder to clean without causing corrosion, its widespread use for medical application is limited. On exposure to air, copper undergoes rapid oxidation which in turn limits its antimicrobial use in aerobic condition.

Conclusion

Bacteria, viruses, and other disease-causing microorganisms are more likely to be found in public places like airports, shopping centres, and hospitals. Since the covid-19 virus that is causing the pandemic is so contagious, it is critical to keep the virus from spreading further. The influence of copper can be summarized as follows,

1. On copper surfaces, the covid-19 virus is active for less than 4 h, compared to plastic and stainless steel on which the virus was present for more than three days.

2. Therefore, if the contact surfaces are made of copper, the spread of the disease would be minimized. In addition, copper is preferred for doorknobs, push plates, handles, stair railings, restroom faucets, and other applications. All of these public surfaces are more prone to spread disease-causing microbes to hands, resulting in infection.

3. Copper has inherent antimicrobial properties. When cleaned thoroughly and on a regular basis, infectious pathogens can be effectively inactivated on regularly touched surfaces made of uncoated copper alloy materials.

4.The exposure of copper to covid-19 has been reported to inactivate viral genomes and showed an irreversible impact on virus morphology, including envelope disintegration and surface spike dispersal.
5. Since corona viruses are structurally similar, copper alloy's anti-coronavirus activity is likely to be effective to all coronavirus strains.

Of course, hand washing, good hygiene, and social distancing remain the most successful ways to fight covid-19 or any such viruses. However, strategic copper usage will complement these steps, allowing the physical environment to effectively combat harmful bacteria and viruses.

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ALCOHOLS AS ALTERNATIVE FUELS : AN OVERVIEW

Project work

Submitted for partial fulfilment of the B.Sc. degree in Chemistry

By

SUBRATA PAL

Under the supervision of Dr. SUBHABRATA BANARJEE

SUBRATA PAL

Registration number: A01-1152-112-040-2019

Department of chemistry

RAMAKRISHNA MISSION VIVEKANANDA CENTENARY COLLAGE

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I am also very much thankful to all our respected teachers, whose valuable teaching and research ideas have continuously motivated me.

I am also thankful to all other respected staff members of our department.

Finally, my deepest admiration goes to my parents for their all-out support throughout my life.

(Full Signature of the Candidate)

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Date : *15th January, 2022*

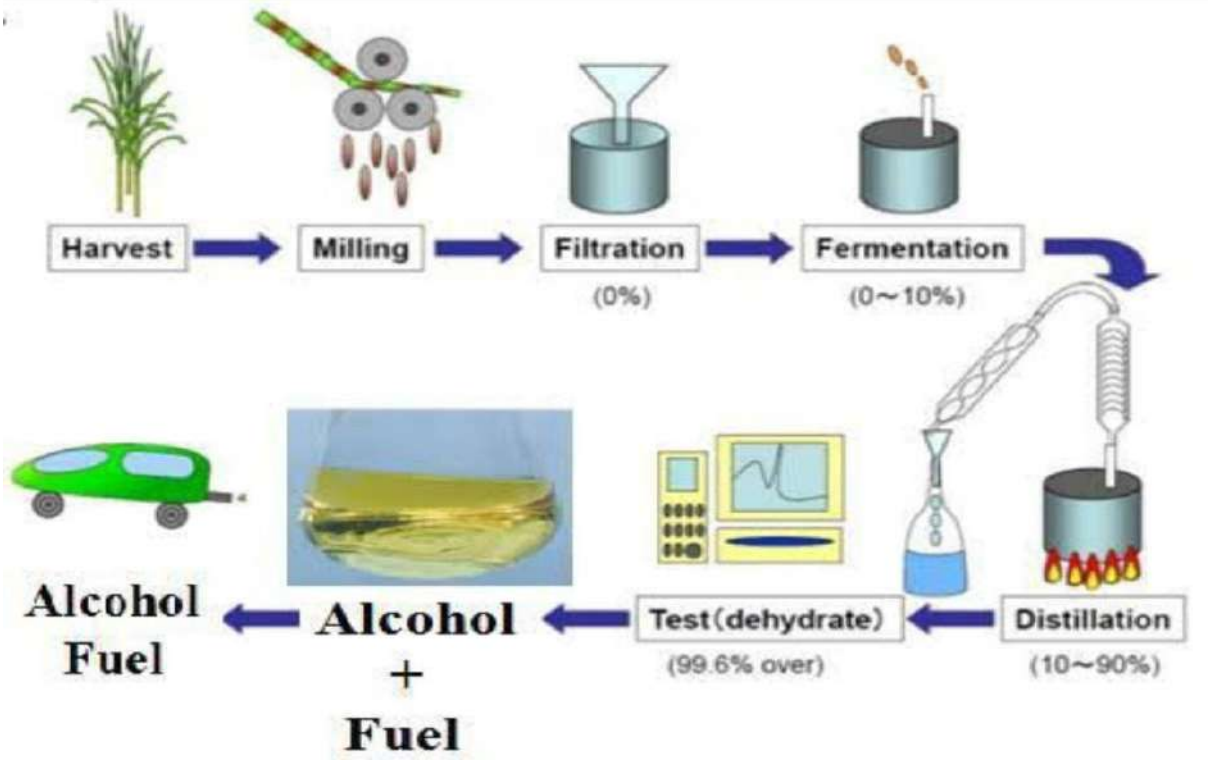
Place : *RAHARA*

ALCOHOLS AS ALTERNATIVE FUELS : AN OVERVIEW

ABSTRACT:

Alcohol type of fuels is **alternative to petroleum-based fuels** due to less greenhouse gas emission, much less toxic exhaust emission and enhancement of overall energy efficiency. Due to the depletion of lead in all petrol grades and the adverse health and environmental effects of MTBE, the synthesis of alcohols, especially ethanol, from synthesis gases, has been significantly attracted interests from the scientific community. Low molecular weight alcohol has been replaced by other additives such as ethanol octane booster in automotive fuel. Due to the presence of oxygen, which increases combustion efficiency and reduces air pollution, adding alcohol to petroleum products allows the fuel to burn more completely. The presence of alcohol in the fuel can cause corrosion in the components of the metallic fuel system. For the purpose of making optimal use of alcohol as an alternative fuel, one can either redesign the engine or the car can be redesigned. Alternatively one can mix one or more additions of ethanol or methanol to improve its properties. The catalytic conversion of synthetic gas to alcohol is convenient, as it utilizes a variety of renewable and non-renewable source of carbon and hydrogen. Different catalytic systems can be used for conversion of synthesis gas into higher alcohol. Depending on the state of the process and the catalyst used, the reaction process varies, and the products include the primary and secondary alcohols (with or without branching). The current study includes a brief overview of the processes and catalysts used depending on the production of certain alcohols, as well as, reaction processes those are currently adopted. Supported Rhodium-based catalysts are thought to be a promising catalyst for improving hydrogenation and linear alcohol production.

INTERODUCTION



Over the past few decades, considerable efforts have been made by the government and industry to provide clean petrol.

Originally, lead was added to gasoline as an octane enhancer. For each one gram of lead added to one gallon of gasoline, the octane rating becomes about 10 times or more than the octane number [**1**]. A certain minimum level of octane is required for smooth running and resistance**.** Concern over knockout lead gasoline emissions prompted Environmental Protection Agency, USA (EPA) to reduce lead in petrol.

Since then unleaded petrol has become the standard and petroleum refineries

have been looking at other additions to help keep petrol octane numbers according to leadership standards.

Aromatics and alcohol have been the most popular choices. Aromatics, such as benzene and toluene, have high octane levels, but the presence of these compounds produces toxic fumes. Besides benzene is very well known carcinogenic compound [**2**]. The EPA has approved the use of several alcohols and ether in unleaded petrol.

Ethanol and methyl tertiary butyl ethers (MTBE) are the two most popular additions. Though MTBE is not used as widely as ethanol, but refineries still use it as an additive . It is not as sensitive to water as other additives and tends not to increase the fuel volatility [**3**]. Gasoline and its fuel properties have a direct impact on the environment. Table 1 gives an overview of gasoline properties, their desired effect, engine performance, and their adverse effects on the environment **[4**]. Low molecular weight alcohols such as ethanol have been replaced by other additions such as octane booster to automotive fuel. Alcohol can be promoted as an alternative fuel or alternative fuel component in transportation for many reasons, e.g.

1) Reduce greenhouse gas emissions
2) Decreased toxic emissions
3) Increase overall energy efficiency
4) Reduce fuel consumption
5) Social factors (e.g., employment in the agricultural sector)

Unlike petrol and diesel, alcohol contains oxygen. Adding alcohol in petroleum products allows the fuel to burn more completely due to the presence of oxygen, which increases combustion efficiency and reduces air pollution. Using petrol

mixed with approximately 10% ethanol can substantially reduce emission of greenhouse gases.

An additional ingredient that makes ethanol attractive as a fuel expander or the alternative fuel is that it is a renewable resource. **Table 2** compare properties of alcohol such as boiling point, latent heat, vapour pressure and solubility in water with octane and hexadecane **[5]**. Alcohol is lower than conventional **fuels** in terms of combustion power. However, the lowest stoichiometric air to fuel ratio helps alcohol fuel to produce more power inside an engine when this fuel is burned. **Table 3** shows the effective blending values of the oxygenated fuel [**6**]. The research octane number (RON) of engines is tested at relatively low speed (600 rpm). This is done to simulate the driving speed in the city with frequent acceleration. Motor octane number (MON) is measured at a high speed (900 rpm), which mimics highway driving. For most fuel components, RON larger than MON and the difference between them is used to judge fuel quality. This is known as fuel sensitivity and the maximum value for petrol is specified, which should usually be less than 10.

TABLE 1:

Table 1
Summary of gasoline properties [4].

Gasoline property	Desirability	Impact on environment
Octane number	Avoid engine knocking; increase fuel–air mix compression ratio, engine power, and efficiency	Octane boosting compounds are not environmentally friendly: – Lead additives are toxic air pollutants and poison catalytic converter catalysts. – Benzene is carcinogenic. – Aromatics produce more smoke and smog – Olefins form engine fouling gums, more smoke and smog
Volatility (Reid vapor pressure)	Sufficient light components to give adequate vaporization of fuel air mix for easy engine cold start	– Too many light components result in hydrocarbon loss & result in atmospheric pollution. – Too many heavy components contribute to chamber deposits & spark plug fouling causing release of unburnt hydrocarbons into the atmosphere.
Sulfur content	Not desirable	– Sulfur compounds are corrosive, foul smelling, and increase sulfur trioxide emissions. – Decreased catalytic converter efficiency. – Adversely affect ignition timing, leading to lower engine efficiency.
Olefins	Desirable for their octane value	– Leads to deposits and gum formation; increased emissions of ozone forming hydrocarbons, and toxic compounds.
Aromatics	Desirable for their octane value	– Increased engine deposits and tailpipe emissions, including carbon dioxide. – Produces carcinogenic benzene in exhaust.
Stability additives	Reduce valve deposits	– Affect carburetors resulting in higher H/C and CO emissions.

TABLE 2:

Characteristics of chemically pure fuels [5].

Fuel	Chemical weight (lb/mol)	Specific gravity	Boiling point (°C)	Latent heat (Btu/lb)	Combustion energy (Btu/lb)	Vapour pressure @100 F (psig)	Solubility part in 100 parts H_2O	Stoichiometric air–fuel ratio
Methanol	32	0.79	65	503	10,260	4.6	Infinite	6.5
Ethanol	46.1	0.79	78	396	13,160	2.2	Infinite	9
Butanol	74.1	0.81	117	186	15,770	0.3	9	11.2
Octane	114	0.70	210	155	20,750	1.72	Insoluble	15.2
Hexadecane	240	0.79	287	-	20,320	3.46	Insoluble	15

TABLE 3:

Effective blending values of the fuels [6].

Fuel	Density (kg/l)	% of O_2 (wt%)	RON	MON	RVP (kPa)
Methanol	0.796	49.9	130	100	250
Ethanol	0.794	34.7	115	100	130
IPA	0.789	26.6	117	100	70
TBA	0.791	21.6	100	90	65
MTBE	0.744	18.2	110	100	55
ETBE	0.770	15.7	112	100	28

Although methanol has the highest percentage of oxygen, compared to ethanol, and higher sensitivity and higher reed vapour pressure (RVP) that other alcohols, it is not preferred. In general, ethanol is more convenient when comparing the percentage of oxygen content, sensitivity, and reed vapour pressure with other fuels.

CATALYST SUPPPORT FOR HIGHER ALCOHOL SYNTHESIS

Rhodium-group catalysts Supported

Hydrogenation of carbon monoxide on transition metal catalysts produce various compounds such as hydrocarbons, alcohol, aldehydes and acids. Catalysis, Over transition metal catalysts, alkali doping inhibits methanol formation and favours the formation of ethanol. In 1978, Ichikawa et al. reported that the C2-oxygenated compounds (mainly ethanol) were produced on an Rh-based catalyst during methanol synthesis. In the eighth group metal, Rh is mainly unique in its ability to catalyze formation of C2 oxygenates from syngas. Rhodium is an element which in most catalytic studies, usually in conjunction with promoters, increase the activity or selectivity of ethanol. In the last decade, research has focused on the characteristics of Rh-based catalysts and on higher alcohol synthesis using them as catalysts. These catalysts are advantageous due to low operating conditions including normal operating 150-250^{o}C temperature and pressure of 0.1-2.5 MPa [**7**]. The addition of transition metals such as Mn, Ti, and Zr in oxide form on Rh/SiO2 enhances the CO conversion rate 10–50 times more than that with Rh/SiO2 alone, and also improves the selectivity towards C2-oxygenates. This is due to oxophilic

promoters Rh is located on the surface of the particle, which increases the rate of CO dissipation and the steady-state coverage of the surface, including alkalis.

The addition of base metals such as Zn and Fe are effective in blocking CO dissociation on the Rh surface and, hence, methanation and C2-oxygenate formation is substantially suppressed [**8**]. The addition of Fe and Mo enhances the chain growth properties Rh / ZrO_2 improves the structure of catalysts and C_{2+} components. Medium response pressure between 0.1 and 2.5 MPa and low temperatures between 150 and 250^oC, favour formation of C_{2+} component. Rh / ZrO_2 is produced by adding Fe to the catalyst. Adverse effects in this case is that It reduces the number of Rh atoms available for CO and hydrogen absorption, increases the number of double-bonds CO (Rh-CO-Fe), and in favour of the formation of oxygenated products. In Rh / ZrO_2 catalysts, iron promotes activity and selection when oxygenated products are in small quantities (Fe / Rh <1.5). But the activity decreases only when it is present in large quantities [**9**]. Supported Rh catalysts in SiO_2 and CeO_2 have been compared in case of CO hydrogenation [**10**]. The main C2 oxygenate formed on SiO_2-supported Rh-catalyst was acetaldehyde, which contained ethanol. Obtained mainly on CeO_2 supported Rh catalyst. It was too observed that CeO_2 suppressed alkene formation to a greater extent than it did C2 oxygenate production, and has improved structure Of methanol.

Table 4

Comparison of the activities of supported Rhodium-group catalysts.

	Reference					
	Wang et al. [47]	Wang et al. [47]	Hu et al. [43]	Guglielminotti et al. [46]	Guglielminotti et al. [46]	Guglielminotti et al. [46]
Catalyst	2 wt% Rh/SiO_2	2 wt% Rh/CeO_2	$Rh\text{-}Mn/SiO_2$	Rh/ZrO_2	$Fe\text{-}Rh/ZrO_2$ (Fe/Rh = 1.5)	$Fe\text{-}Rh/ZrO_2$ (Fe/Rh = 2.0)
Temperature (°C)	180	180	280	220	220	220
Pressure (MPa)	0.1	0.1	5.4	0.1	0.1	0.1
H_2/CO molar ratio	2.0	2.0	2.0	3.0	3.0	3.0
GHSV (l/kg_{cat} h) *(h^{-1})	9000	9000	*3750	6000	6000	6000
CO conversion (%)	-	-	25	6	9	6
STY of total oxygenates ($\mu mol\ C/g_{cat}$ min) *(mmol CO/g_{Rh} min)	0.676	0.137	-	*12	*21	*13
STY of C_2 oxygenates ($\mu mol\ C/g_{cat}$ min)	0.663 (mainly acetaldehyde)	0.090 (mainly ethanol)	-	-	-	-
Total oxygenate selectivity (% of C)	23	58	61	14	27	21
Hydrocarbon selectivity (% of C)	77	42	39	81	69	75

SOME REACTIONS FOR HIGHER ALCOHOL SYNTHESIS

Support Rh-based catalysts

Xiaoding et al. suggested the following reaction scheme for the production of higher alcohol from syngas over Rh-based catalysts

$$\tfrac{1}{2}H_2 + s \rightarrow H_s$$

$$CO + s \rightarrow CO_s$$

$$CO + s \rightarrow C_s + O_s$$

$$C_s + xH_s \rightarrow (CH_x)_s$$

$$CH_3 + (CH_x)_s \rightarrow (C_2H_y)_s$$

$$(C_nH_z)_s + (CH_x)_s \rightarrow (C_{n+1}H_{x+z})_s$$

$$(C_{n+1}H_{x+z})_s + H_s \rightarrow C_{n+1}H_{2n} + H_s \rightarrow C_nH_{2n+2}$$

$$(C_nH_z)_s + CO_s \rightarrow C_nH_zCO_s + H_s \rightarrow C_{n+1}H_{2n+3}OH$$

The hydrogenation of CnHzs leads to the formation of alkanes and alkenes, whereas, Cos insertion to CnHzs leads to the formation of CnHzCOs species.

Conclusions:

Ethanol synthesis is of interest due to increasing petroleum prices, environmental concerns. The presence of ethanol in the claimed fuel causes decay of metallic fuel system components and locks engine steam due to high steam pressure and low boiling point. This can be avoided by redesigning the engine or mixing the additives, such as higher alcohol, to improve fuel properties. Catalytic conversion of synthesis gas to alcohol is convenient because it uses a variety of renewable and non-renewable carbon resources. Different catalytic systems can be used for obtaining high alcohol from Synthesis

gas. The process depends on the conditions and the catalyst used. The reaction process varies and the products contain both primary and secondary alcohols (with or without branching). Supported Rhodium-based catalysts are thought to be a more promising choice for CO hydrogenation and linear alcohol production.

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ALCOHOLS: AN ALTERNATIVE FUEL

Project Work

Submitted for Partial Fulfillment of the B.Sc. Degree in Chemistry

By

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Place: Kolkata

Date: 20th January, 2022

ALCOHOLS: AN ALTERNATIVE FUEL

ABSTRACT:

Due to the phase out of lead in all gasoline grades and the adverse health and environmental effects of MTBE, the synthesis of higher alcohols, particularly ethanol, from synthesis gas has drawn considerable interest. Low molecular weight alcohols such as ethanol have replaced other additives as octane boosters in automotive fuels. Adding alcohols to petroleum products allows the fuel to combust more completely due to the presence of oxygen, which increases the combustion efficiency and reduces air pollution. The presence of alcohols in fuel causes corrosion to metallic fuel system components. In order to make the best use of alcohols as alternative fuels; one can redesign the engine or the vehicle can be redesigned or one can blend in one or more additives to the ethanol or methanol to improve its characteristics. Catalytic conversion of synthesis gas to alcohols is advantageous, as this uses various renewable and non-renewable carbon resources. Different catalytic systems can be used for synthesizing higher alcohols from synthesis gas. Depending on the process conditions and the catalyst used, the reaction mechanism varies and the products include primary and secondary alcohols of both normal and branched carbon chains. The present paper includes an overview of the processes and catalysts used depending on the production of specific alcohols, as well as, the reaction mechanisms currently accepted. Transition metal-promoted alkali-modified molybdenum sulphide catalysts are considered to be a promising class of catalysts to improve CO hydrogenation and for the production of linear alcohols.[1]

INTRODUCTION

Over the past decade, considerable effort by government and industry has been directed towards providing cleaner gasoline. Originally, lead was added to gasoline as an octane enhancer. For each gram of lead added to a gallon of gasoline, the octane rating goes up about 10 times or more in octane numbers [2]. Engines require certain minimum levels of octane to run smoothly and resist knocking. Concern about leaded gasoline emissions encouraged the Environmental Protection Agency, USA (EPA) to call for reduced lead in gasoline. As unleaded gasoline became the standard, petroleum refineries looked to other additives to help keep gasoline octane numbers at leaded standards. Aromatics and alcohols [**Table-1**] have been the most popular choices. Aromatics, such as benzene and toluene, have high octane levels, but the presence of these compounds produces more smoke, smog. Besides benzene is a well-known carcinogenic compound [3]. The EPA has approved using several alcohols and ethers in unleaded gasoline. Ethanol and methyl tertiary butyl ethers (MTBE) are the two most popular additives. MTBE is not as widely used as ethanol, but refineries use it as an additive because it is not as sensitive to water as other additives and tends not to increase fuel volatility [4]. The fuel properties of gasoline and its contents have a direct impact on the environment. **Table 2**[5] gives a brief account of gasoline properties, their desirable impact on engine performance, and their undesirable impact on the environment[5].

Low molecular weight alcohols such as ethanol have replaced other additives as octane boosters in automotive fuels. Alcohols can be promoted as alternative fuels or alternative fuel components in transportation for many reasons, such as:

- Reduction of greenhouse gas emissions
- Reduction of toxic exhaust emissions
- Enhancement of overall energy efficiency
- Reduction of fuel costs
- Societal reasons (e.g., employment in the agricultural sector)

(Million US gallons per year)				
According to 2017 worldwide ranking	**Country/Provence**	**2014 (Million US gallons)**	**2015 (Million US gallons)**	**2016 (Million US gallons)**
1	U.S	14,300	14,806	15,330
2	Brazil	6,190	7,093	7,295
3	European Union	1,445	1,387	1,377
4	China	635	813	845
5	Canada	510	436	436
6	Thailand	310	334	322
7	Argentina	160	211	264
8	India	155	211	225
******	Remaining the world	865	391	490
******	Throughout the world	24,570	25,682	26,094

Table-1: Annual production alcohol fuel from different countries in the year of 2014-2016 [54]

Table- 2: Summary of Gasoline properties. [5]

Gasoline property	Desirability	Impact on environment
Octane number	Avoid engine knocking; increase fuel–air mix compression ratio, engine power, and efficiency	Octane boosting compounds are not environmentally friendly: – Lead additives are toxic air pollutants and poison catalytic converter catalysts. – Benzene is carcinogenic. – Aromatics produce more smoke and smog – Olefins form engine fouling gums, more smoke and smog
Volatility (Reid vapor pressure)	Sufficient light components to give adequate vaporization of fuel air mix for easy engine cold start	– Too many light components result in hydrocarbon loss & result in atmospheric pollution. – Too many heavy components contribute to chamber deposits & spark plug fouling causing release of unburnt hydrocarbons into the atmosphere.
Sulfur content	Not desirable	– Sulfur compounds are corrosive, foul smelling, and increase sulfur trioxide emissions. – Decreased catalytic converter efficiency. – Adversely affect ignition timing, leading to lower engine efficiency.
Olefins	Desirable for their octane value	– Leads to deposits and gum formation; increased emissions of ozone forming hydrocarbons, and toxic compounds.
Aromatics	Desirable for their octane value	– Increased engine deposits and tailpipe emissions, including carbon dioxide. – Produces carcinogenic benzene in exhaust.
Stability additives	Reduce valve deposits	– Affect carburetors resulting in higher H/C and CO emissions.

Unlike gasoline and diesel, alcohols contain oxygen. Adding alcohols to petroleum products allows the fuel to combust more completely due to the presence of oxygen, which increases the combustion efficiency and reduces air pollution. Using gasoline blended with 10% ethanol can reduce greenhouse gas emissions. An additional factor making ethanol attractive as a fuel extender or substitute is that it is a renewable resource. **Table 3**[6] compares the properties of alcohols such as boiling point, latent heat, vapour pressure and solubility in water, with those of octane and hexadecane [6]. Compared to conventional fuels, alcohols have less combustion energy. However, the lowest stoichiometric air to fuel ratio helps alcohol fuels to produce more power inside an engine when these fuels are burned.

Table- 3: Charecteristics of Chemically pure Fuels. [6]

Fuel	Chemical weight (lb/mol)	Specific gravity	Boiling point (°C)	Latent heat (Btu/lb)	Combustion energy (Btu/lb)	Vapour pressure @100 F (psig)	Solubility part in 100 parts H_2O	Stoichiometric air-fuel ratio
Methanol	32	0.79	65	503	10,260	4.6	Infinite	6.5
Ethanol	46.1	0.79	78	396	13,160	2.2	Infinite	9
Butanol	74.1	0.81	117	186	15,770	0.3	9	11.2
Octane	114	0.70	210	155	20,750	1.72	Insoluble	15.2
Hexadecane	240	0.79	287	-	20,320	3.46	Insoluble	15

Table 4 [7] shows the effective blending values of oxygenated fuels as gasoline blends [7]. Research Octane Number (RON) is determined in test engines at a relatively low speed (600 rpm) to simulate city driving speed with frequent acceleration. Motor octane number (MON) is measured at a higher speed (900 rpm), which simulates highway driving. For most fuel components, RON is greater than MON and the difference between them is used to judge fuel quality. This is known as the sensitivity of the fuel and a maximum value is specified for the gasoline, which typically should be less than 10. Although methanol has the highest percentage of oxygen, its sensitivity is 30 when compared with ethanol, having a sensitivity of 15 and a Reid vapour pressure (RVP) much less than that of methanol. In essence, ethanol is more advantageous when comparing the percent oxygen content, sensitivity, and Reid vapour pressure with those of other fuels.

Table- 4: Effective Blending Values of the Fuels. [7]

Fuel	Density (kg/l)	% of O_2 (wt%)	RON	MON	RVP (kPa)
Methanol	0.796	49.9	130	100	250
Ethanol	0.794	34.7	115	100	130
IPA	0.789	26.6	117	100	70
TBA	0.791	21.6	100	90	65
MTBE	0.744	18.2	110	100	55
ETBE	0.770	15.7	112	100	28

RESULTS & DISCUSSION / SUMMARY OF THE WORK:

1. Adverse Effects of Alcohol Fuels

The importance of alcohols as a fuel is immense. But there are some adverse effects of the alcohol fuels.

The presence of alcohols in fuel causes corrosion to metallic fuel system components because of increased water content in the fuel and partly because of the organic acids produced in commercial oxygenates. Other major disadvantages of alcohol fuels are vapour lock due to their higher vapour pressures and lower boiling points [8]. The major difference between the alcohols and gasoline is that alcohols are strong solvents and, hence, highly corrosive to some metal parts of the engines. Methanol is more corrosive compared with higher alcohols. There is limited miscibility between methanol and gasoline, due to the presence of minute amounts of water, which causes phase separation. When compared to methanol, ethanol has lower vapour pressure, better solubility with hydrocarbon liquids, improved water tolerance, and higher overall heating value. Other redeeming qualities such as latent heat of vaporization, volatility, and anti-knock values make ethanol fuels superior to methanol blended fuels [9]. Phase separation occurs when alcohol and water mix together in an ethanol blended fuel. When the alcohol and water get separated from the gasoline, the resulting mixture settles at the bottom of the tank and becomes corrosive [10]. Corrosion due to alcohols is of three types: general corrosion, dry corrosion and wet corrosion. General corrosion is due to ionic impurities such as chloride ions and acetic acid. Dry corrosion is due to the polarity of the ethanol molecule. The azeotropic formation of ethanol and water causes wet corrosion. Ethanol with almost neutral pH has little corrosive effect. If the alcohol/gasoline blend stays for a sufficiently large time inside the tank, it allows the alcohol to absorb moisture from the atmosphere and causes corrosion to the fuel injection

system. Non-metallic components such as seals and O-rings in the fuel injection system tend to swell and stiffen due to the presence of alcohols in fuels [11].

2. Modifications required for the best use of alcohol fuels

In order to best use the alcohols as alternative fuels there are two options: redesign the engine to take full advantage of the properties of the alcohol or blend in one or more additives to the ethanol or methanol to improve its characteristics.

2.1. Modifications to vehicles

The following modifications are typical for converting conventional vehicles to high-level alcohol blends [12].

1. Stainless steel fuel tank with stainless flame arrestors in the fill and vent tubes to prevent ignition by an external source.
2. Methanol resistant float level potentiometer with a corrosion protection circuit.
3. Higher flow methanol–tolerant fuel injector and fuel pump to handle higher flow rates.
4. Stainless fuel lines with accompanying Teflon fuel hoses.
5. Anodized aluminium fuel injection rail and modified pressure regulator.

2.2. Additives required for improving the fuel properties of alcohols

Alcohols can be used effectively as alternative liquid transportation fuels by modifying their properties by using certain additives, which must be physically and chemically compatible with the base alcohol fuel and have the same or higher specific energy content. Additives must not be readily removable from the fuel, must not significantly add to exhaust emissions, or should not leave any undesirable residue. They should not further create any complication and they should be relatively inexpensive[13].

Ethanol and methanol are completely miscible with water, but show very poor miscibility with gasoline containing traces of water. So, blending gasoline with ethanol or methanol in the presence of water may lead to a phase separation problem. Additives such as higher alcohols like iso-propanol, 1-butanol, n-decanol, various commercial non-ionic surfactants, and various anionic fatty acid surfactants can effectively minimize the phase separation problem. The prevention of phase separation would improve overall drivability and prevent corrosion of water-sensitive metallic components of the engine such as aluminium [14].

Conventional fuel injection systems usually encounter lubrication problems due to the low viscosity of alcohol fuels, which leads to wearing of the engine parts. Higher alcohol additives offer better lubrication and decrease wear in engine parts. During combustion, alcohol blended fuels produce acids that are responsible for wearing of engine parts. Neutralizers such as zincdialkyldithiophospates and calcium sulfonates are added in lubricant oil to neutralize these acids and improve lubrication. Shorter intervals of lubricant oil change can reduce corrosive wear significantly [15].

3. Production of industrial ethanol

Ethanol can be manufactured by

1. Fermentation of sugar derived from grain starches (wheat and corn), sugar beets, or sugar crops using microorganisms.
2. Using surplus wine ethanol; fermentation of the non-sugar lignocellulose fractions of crops (grasses and trees).
3. Synthetically, through direct hydration of ethylene (derived from petroleum).
4. High temperature catalytic conversion of synthesis gas to liquid fuels by the Fischer–Tropsch process to produce a mixture of alcohols.

   [The chemical reactions for the fermentation of carbohydrates to ethanol in the presence of yeast are [16]:

   $$C_{12}H_{22}O_{11} + H_2O \rightarrow 2C_6H_{12}O_6 \quad (1)$$

   $$C_6H_{12}O_6 \rightarrow 2CH_3CH_2OH + 2CO_2 \quad (2)$$

   Another method of manufacturing ethanol is reacting ethylene with steam. The catalyst used is solid silicon dioxide coated with phosphoric (V) acid. The reaction is reversible.

   $$CH_2 = CH_2 + H_2O \leftrightarrow CH_3CH_2OH;\ H = -45\ \text{MJ/kg mol} \quad (3)]$$

4. Synthesis of higher alcohols from synthesis gas

The synthesis of higher alcohols from synthesis gas by direct catalysis was recognized in 1923 by Frans Fischer and Hans Tropsch. They reported that a mixture of alcohols, aldehydes, ketones, fatty acids, and esters were formed when the reaction between CO and H_2 was performed at pressures ranging from 10 to 14 MPa and at temperatures of 400–500 ^oC in the presence of an alkalized iron oxide catalyst. They named the mixture synthol and named the process the synthol process [17]. In 1930, Frolich and Cryder reported the formation of alcohols higher than methanol by passing syngas over a Zn:Mn:Cr, 1.0 : 1.1 :

1.03 catalyst. They reported that methanol is formed from a formaldehyde intermediate and that the higher alcohols are formed from the methanol through a stepwise condensation reaction [18]. In the 1940s, Du Pont developed an alkalized Mn-Cr catalyst to synthesize methanol and higher alcohols from syngas for commercial purposes [19]. In the late 1940s, Farbenindustrie et al. introduced the Synol process for the manufacture of alcohols from syngas. This process uses low pressures of around 2 MPa with higher productivity of alcohols by modifying the Fischer–Tropsch alkalized iron catalyst [20]. Natta et al. reviewed the synthesis of higher alcohols from CO and H_2, in 1957 and reported that the synthesis of higher alcohols was always related to the presence of strongly basic substances [21].

5. Catalyst systems for higher alcohols synthesis

Several authors summarized typical operating conditions, research status, characteristics, and performance of primary groups of catalysts that have been adapted and tested for higher alcohol synthesis (HAS)[1] . According to these reviews, there are two major catalyst groups for higher alcohol production:

5.1. Modified methanol synthesis catalysts

a. Alkali-modified high pressure, high temperature methanol synthesis catalysts.
b. Alkali-modified low pressure, low temperature methanol synthesis catalysts.

5.2. Modified Fischer–Tropsch catalysts

a. Fe, Ni, or Co-modified low temperature, low pressure methanol synthesis catalysts.
b. Supported rhodium-group catalysts.
c. Alkali-modified molybdenum-based catalysts.

5.3. High pressure, high temperature methanol synthesis catalysts

The alkali-modified molybdenum-based catalyst is being considered here:

6. Alkali-modified molybdenum-based catalysts

The sulfides of transition metals have been used in the petroleum industry in hydrodesulfurization, hydrodenigrodenation, and hydrogenation reactions for over 50 years. Molybdenum disulfide (MoS_2) when supported with an alkali can be used as a catalyst for the production of alcohols from syngas. The commercial Mo-based catalysts to convert synthesis gas to alcohols were first developed by Dow and Union Carbide companies. The

functions of alkali are to reduce the hydrogenation ability of alkyl species to form alkanes and to increase the active sites for the formation of alcohols [22,23]. Alkali-modified molybdenum-based catalysts are more attractive due to their excellent resistance to sulfur poisoning and their high activity for water–gas shift reaction. This saves the cost of ultra-desulfurization for feed gas and separation of water [24]. The alcohol products over these catalyst systems are linear alcohols, and the mechanism for formation of higher alcohols ($C_{2+}OH$) was via a classical insertion of CO into the corresponding precursor alcohol. The activity and selectivity to $C_{2+}OH$ was found to be low due to A-S-F distribution [25]. The effect of CO hydrogenation reaction towards the formation of higher alcohols also depends on the catalyst support.

Table 5 compares the activities of alkali-modified molybdenum-based catalysts supported on various supports [24,26-30]. The catalytic performance of alkali-modified molybdenum-based catalysts supported on carbon-based supports such as, activated carbon (AC) and multi-walled carbon nano-tubes (MWCNTs) were found to be high in terms of higher alcohols yield and selectivity compared to that of unsupported and catalysts supported on metallic oxide supports, such as SiO_2 and Al_2O_3.

The F-T elements such as Ni and Co increase the alcohol yield and selectivity towards higher alcohols of MoS_2 catalysts [31,32]. The presence of Co in alkali-modified MoS_2 catalysts enhanced the $C_1 \rightarrow C_2$ homologation step that led to ethanol as the dominant product[33]. The addition of Nickel to K/MoS_2 catalysts leads to methanation [31]. The addition of Mn on Ni/K/MoS_2 catalysts inhibits the enrichment of Ni to a certain extent, which restrains the formation of hydrocarbons and carbon chain growth promoted by Ni, leading to improved selectivity of higher alcohols [34]. The typical operating temperature and pressure are in the range of 250–350 ^oC and 5–10 MPa [35].

Increasing the reaction temperature increases the selectivity of both hydrocarbons and higher alcohols, but decreases the selectivity of methanol. The promoting effect of different alkali metals (K, Rb, and Cs) on MoS_2 catalyst for the formation of higher alcohols depends on the alkali : Mo ratio. The performance of K and Rb are superior to those of Cs at an alkali : Mo ratio of 0.7:1.0. The performance for Cs-promoted catalysts can be improved by decreasing the ratio from 0.7:1 to 0.22:1 [36]. The promotional effect of K was greater than Cs for alcohol synthesis over the Co-MoS_2/clay catalyst [37]. The addition of Cl has no

Table-5: Comparison of the activities of alkali-modified molybdenum-based catalysts.

	Wooetal. [26]	Bianetal. [27]	Muramatsu etal. [28]	Lietal. [29]	Lietal. [30]	Surisettyetal. [24]
Catalyst	Mo-K	Mo-K/Al_2O_3	Mo-K/SiO_2	Mo-K/AC	Mo-K/AC	Mo-K/MWCNT
Temperature(°C)	300	310	200	330	320	320
Pressure(MPa)	5.0	5.0	1.6	5.0	8.0	9.7
H_2/CO molar ratio	1.7	1.7	1.0	2.0	1.0	2.0
GHSV(h^{-1}) *(mol/kg_{cat} h)	*139	4800	*100	7200	2500	3600
CO conversion(%) **CO_2-free CO conversion(%)	13	**3	11	13	23	33
STYof total alcohols(g/g_{cat} h) ***(COmol/kg_{cat} h) ****(g/ml_{cat} h)	90[a]	0.017	0.022	***23.1	****0.120	0.11
STYof higher alcohols(g/g_{cat} h) †(COmol/kg_{cat} h) ††(g/ml_{cat} h)	49[a]	0.003	–	†12.1	††0.066	0.062
Total alcohols selectivity(%of C) †††(%ofCO)	71(CO_2-free)	36	–	†††38	51(CO_2-free)	25
Hydrocarbon selectivity(%of C)	29(CO_2-free)	–	–	–	49(CO_2-free)	30

[a] Activity was normalized for an initial activity of 100%

promotion effect on alcohol activity, but increases the selectivity of alcohol formation. The presence of carbon-dioxide in the feed causes greater amounts of water to be produced, but reduces the formation of CO_2. The addition of CO_2 reduces the formation of higher alcohols; while H_2S increases the formation of hydrocarbons [38]. Co-promotion to Mo-K catalysts increased the alcohol ratios of C_{2+}/C_1 in the products relative to that for the un-promoted sample. Co species show a relatively stronger interaction with the Mo component in the form Co–Mo–S structure than the in Co–Mo–O structure [32]. Mo species with intermediate valence (around +3.5) are more active phases for alcohol synthesis from CO hydrogenation, while those with lower Mo valence are responsible for the production of hydrocarbons [39].

Depending on the reaction conditions, and on the properties of alkali promoters, and support, Rh-species in catalysts are capable of catalyzing dissociation, insertion, and hydrogenation of CO [40]. The conversion of CO and the yield of oxygenates over Mo-Rh/Al_2O_3 catalysts is high when compared to Rh/Al_2O_3 catalysts [41]. The interaction of rhodium with molybdenum affects the status of the rhodium species, which affects CO adsorption. The formation of alcohols on rhodium catalysts can be catalyzed by the sites that are less electron-rich than those needed for hydrocarbons, and more of these electron-deficient sites can be created by the interaction of rhodium with molybdenum [42,43]. The incorporation of rhodium into the K-promoted MoS_2 catalysts increases catalytically active surfaces and is responsible for increasing the activity for alcohol synthesis. Due to the co-existence of cationic and metallic rhodium species stabilized by the interaction of rhodium with molybdenum species, the selectivity to the formation of higher alcohols is high [44].

The effects of promotion of various transition metals on alkali-modified MoS_2 catalysts for higher alcohols synthesis are compared in **Table- 6**[34,40,42,45-49]. It can be observed from this table that addition of transition metals such as Ni, Co, and Rh to alkali-modified molybdenum-based catalysts significantly improved CO hydrogenation and resulted in enhanced space time yields of methanol, higher alcohols, and hydrocarbons [34,40,42,45-47]. The formation of hydrocarbons is greatly reduced using alkali-modified tri-metallic catalysts supported on MWCNTs compared to that of bimetallic catalysts [48]. The mesoporous activated carbon-supported tri-metallic catalysts showed less activity and selectivity compared to the MWCNT-supported catalysts [49].

Table 6: Comparison of the activities of alkali-modified molybdenum-based catalysts promoted with transition metals

	Qietal.[34]	Lietal.[45]	Lietal.[40]	Surisetty etal.[46]	Surisetty etal.[42]	Surisetty etal.[48]	Surisetty etal.[49]
Catalyst	Ni-Mo-K/AC	Co-Mo-K/AC	Rh-Mo-K/Al_2O_3	Co-Mo-K/MWCNT	Rh-Mo-K/MWCNT	Rh-Co-Mo-K/MWCNT	Rh-Co-Mo-K/AC-Meso
Temperature(◦C)	330	330	327	330	330	330	330
Pressure(MPa)	10.0	5.0	4.0	8.3	8.3	8.3	8.3
H_2/CO molar ratio	2.0	2.0	2.0	1.0	1.0	1.0	1.0
GHSV(l/kg_{cat} h) *(h^{-1})	*3000	*4800	*4800	3600	3600	3600	3600
COconversion(%)	25	14(CO_2-free)	4(CO_2-free)	45	45	49	45
STYoftotal alcohols(g/g_{cat} h) *(g/ml_{cat} h) **(ml/g_{cat} h)	*0.300	**0.199	**0.062	0.236	0.244	0.261	0.202
STYof higher alcohols(g/g_{cat} h) *(g/ml_{cat} h) **(ml/g_{cat} h)	*0.180	**0.114	**0.044	0.171	0.192	0.227	0.096
STYof hydrocarbon(g/g_{cat} h) *(g/ml_{cat} h) **(ml/g_{cat} h)	26(CO_2-free)	–	–	0.395	0.348	0.276	0.275
Total alcohols selectivity(%ofC)	74(CO_2-free)	47(CO_2-free)	59(CO_2-free)	32	33	43	28

7. Catalyst preparation and pre-treatment conditions

In a heterogeneous chemical reaction, the activity and selectivity of products also depend on the selection of precursors and the method of preparation of the catalyst. The selection of precursors has a direct impact on the cost and availability of the chemicals. The deposition of the metals on the support plays an important role in such a way that every metal atom is accessible to the reactants [50]. The catalysts for higher alcohols synthesis can mostly be prepared by sequential pore volume impregnation or incipient wetness method [51]. The catalysts, synthesized in the form of a metal oxide, are subjected to a pre-treatment prior to higher alcohols synthesis. The temperature, pressure, heating rate and pre-treatment gas environment can influence the surface area and the activity of the catalyst [52].

8. Reaction mechanism for higher alcohol synthesis

Depending on the process conditions and catalyst used, alcohols are synthesized using iso-synthesis, variants of Fisher–Tropsch synthesis, oxo-synthesis involving the hydroformylation of olefins, and homologation of methanol and lower molecular weight alcohols to make higher alcohols. The products include primary and secondary alcohols of both normal and branched carbon chains. Other oxygenates such as esters, aldehydes, and ketones are also formed. The following are the chemical reactions [1] involved in the synthesis of higher alcohols from synthesis gas:

$$CO + 2H_2 \leftrightarrows CH_3OH \quad (4)$$

$$CO + H_2O \leftrightarrows CO_2 + H_2 \quad (5)$$

$$CH_3OH + CO + 2H_2 \leftrightarrows CH_3CH_2OH + H_2O \quad (6)$$

$$C_nH_{2n+1}OH + CO + 2H_2 \leftrightarrows CH_3(CH_2)_nOH + H_2O \quad (7)$$

$$2CH_3OH \leftrightarrows CH_3CH_2OH + H_2O \quad (8)$$

$$2CH_3OH \leftrightarrows (CH_3)_2CO + H_2O \quad (9)$$

$$CH_3OH + CO \leftrightarrows CH_3CHO + H_2O \quad (10)$$

$$(CH_3)_2CO + H_2 \leftrightarrows (CH_3)_2CHOH + H_2O \quad (11)$$

$$2CH_3CHO \leftrightarrows CH_3COOCH_2CH_3 \quad (12)$$

Together with these reactions, undesired side reactions such as hydrocarbon formation may occur, especially that of methane.

$$CO + 3H_2 \leftrightarrows CH_4 + H_2O \quad (13)$$

The water gas shift reaction, **Equation (5)**, is assumed to be in thermodynamic equilibrium. According to the reaction stoichiometry, the optimum H_2/CO ratio is 2; however, the simultaneous occurrence of water gas shift reaction means that the optimum ratio is closer to 1. As all the above reactions are exothermic reactions, from a thermodynamic point of view, lower temperatures and higher pressures are profitable for the formation of alcohols.

8.1. Alkali-modified MoS_2 catalysts

Santiesteban et al. [53] developed the reaction system for the production of mixed alcohols from syngas over alkali-modified MoS_2 catalysts based on a CO insertion mechanism. This reaction scheme can be represented in terms of chain initiation, propagation and termination as follows:

Chain initiation:

$$CO + s \leftrightarrows CO_s \quad (14)$$

$$H_2 + 2\,s \leftrightarrows 2H_s \quad (15)$$

$$CO_s + H_s \leftrightarrows CHO_s + s \quad (16)$$

$$CHO_s + H_s \leftrightarrows CH_2O_s + s \quad (17)$$

$$CH_2O_s + H_s \leftrightarrows R_1O_s + s \quad (18)$$

Chain propagation:

$$R_iO_s + CO_s \rightarrow R_iCOO_s + s \quad (19)$$

$$R_iO_s + 2H_s \rightarrow R_{is} + H_2O + 2s \quad (20)$$

$$R_{is} + CO_s \rightarrow R_iCO_s + s \quad (21)$$

$$R_iCO_s + 2H_s \rightarrow R_{i+1}O_s + 2s \quad (22)$$

Chain termination:

$$R_iO_s + H_s \leftrightarrows R_iOH + 2s \quad (23)$$

$$R_iCOO_s + Hs \rightarrow R_iCOOR_{i-1} + 2s \quad (24)$$

$$R_{is} + H_s \rightarrow C_iH_{2i+2} + 2s \quad (25)$$

$$R_{is} \rightarrow C_iH_{2i} + H_s \quad (26)$$

Reactions represented by **Equations (14) – (18)** are assumed to be in equilibrium. R indicates an alkyl group, i.e., $R_i = C_iH_{2i+1}$. Alcohols are formed by hydrogenation of their precursors R_iO_s, hydrocarbons from R_{is} and esters from R_iCOO_s by CO insertion and hydrogenation. Together with the above reactions, a water gas shift reaction also takes place as given by **Equation (5)**.

CONCLUSIONS

Ethanol synthesis is of interest due to the increasing petroleum prices, environmental concerns, and gasoline additive octane demands. The presence of ethanol in the fuel causes corrosion of the metallic fuel system components and causes vapour lock of the engine due to high vapour pressures and low boiling points. This can be avoided by redesigning the engine or blending additives, such as higher alcohols, to improve fuel characteristics. Catalytic conversion of synthesis gas to alcohols is advantageous as this uses various renewable and non-renewable carbon resources. Different catalytic systems can be used for synthesizing higher alcohols from synthesis gas. Depending on the process conditions and catalyst used, the reaction mechanism varies and the products include primary and secondary alcohols of both normal and branched carbon chains. Transition metal-promoted alkali-modified molybdenum sulphide catalysts are considered to be a promising choice to improve CO hydrogenation and for the production of linear alcohols. In the recent past, more and more countries have increased their alcohol fuel production in order to achieve a pollution free World, and, also to make the world a greener and better place to live.

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A REVIEW

ON

ANTIVIRAL PROPERTY OF COPPER AND ITS ALLOYS TO INACTIVATE COVID-19

Project Work Submitted for Partial Fulfillment of the B.Sc. (Honours) Degree in Chemistry

BY

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ANTIVIRAL PROPERTIES OF COPPER AND ITS ALLOYS TO INACTIVATE COVID-19

Abstract

Copper (Cu) and its alloys are prospective materials in fighting covid-19 viral and several microbial pandemics, due to their excellent antimicrobial property. Several studies conducted on copper and its alloys have proven that copper-based alloys possess excellent potential to control the spread of infectious disease. Moreover, recent studies indicate that these alloys can effectively inactivate covid-19 virus. In this project antimicrobial property of copper and copper-based materials are discussed along with their effectiveness of covid-19 with mechanism. This study shows how copper, nanomaterials of copper and copper-coating surfaces affect on microbial growth. Overall, how copper-based materials can be propitiously used as a part of preventive and therapeutic strategies in the fight against covid-19 virus.

Introduction

This project especially shows how covid-19 and other viruses affect the health. Covid-19 is a type of coronavirus. There are many types of viruses and some cause disease. A coronavirus identified in 2019, SARS-CoV-2, has caused a pandemic respiratory illness, called covid-19.

Researchers know that coronavirus is spread through droplets and virus particles released into the air when an infected person breathes, talks, coughs or sneezes. Larger droplets may fall to the ground or surfaces in a few seconds, but tiny particles can linger in the air and accumulate in indoor places, especially where many people gathered and there is poor ventilation. This is why mask wearing, hand sanitizing and physical distancing are essential to prevent covid-19. The first case of covid-19 was reported in Dec 1, 2019 and the cause was a then-new coronavirus later named SARS-CoV-2.

In this review, I will discuss how copper contact affects covid-19 virus along with other viruses, how microbial growth is affected by copper and so on. I will compare other material with copper and then will draw a conclusion.

History of Copper usage in Medicine

Copper has many special properties and has a great effect on our immune system. One of them is antiviral property. Any virus or microbes can't live in copper surface more than 4 hrs. Copper had a great usage in ancient civilization. It would be used in many medical purposes. In ancient Egypt copper and its derivatives were used for water sterilization. In Roman civilization it was used to cure headache, intestinal worms, infections in ear and for general hygiene. Copper-based materials were also used for the treatment of ulceration in Greece. Copper dust along with honey had a great application in antiseptic purposes. In ancient India copper dust was a common material to use as medicinal element.

Use of "Tamra Patra" is also described in Chakra Samhita. In 19th and 20th century for the treatment of many diseases like chronic adenitis, scrofulosis, syphilis, impetigo, lupus, cholera, tubercular infections, eczema and facial neuralgia etc. copper was used. Before 1932, when antibiotics were prepared, it had been used as antimicrobial agent. Researchers showed that in the treatment of anaemia copper is more effective than iron.

Effect of Copper Content/Deficiency on Health

Cardiovascular disease and osteoporosis

Copper has a great effect in our digestion system (Fig. 1). Copper is an essential nutrient for the body. Together with iron it enables the body to form RBC. It maintains healthy bones, blood vessels, nerves, and immune function and it contributes to iron absorption. Sufficient copper (about 2.6 mg/day) may help prevent.

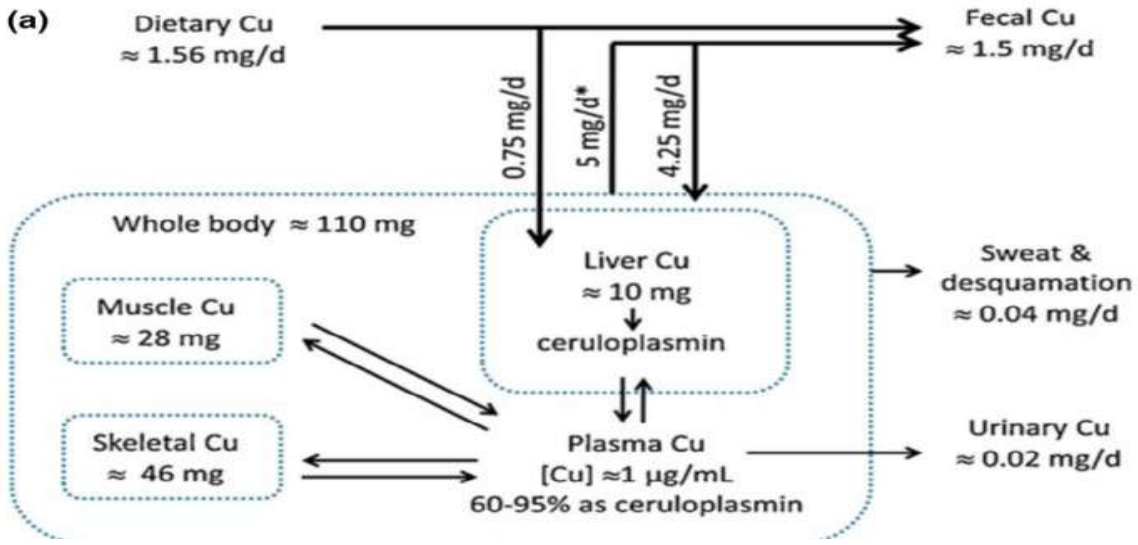

Fig. 1. Copper absorption by various organs.

Due to deficiency of copper different types of diseases like cardiovascular, pulmonary neuronal, skeletal, immunological and behavioural function in offspring during infancy and beyond may appear. Copper deficiency may lead to parasitic infections affecting T-lymphocytes, monocytes, neutrophil and T-cell functions. Thus cell-mediated immunity gets affected. Functions of B-cell, T-helper cell and natural killer cells (phagocytes or macrophages) are inhibited. Moreover, it affects the generation of pathogen specific antibodies.

Antiviral Mechanism of Copper

Copper's toxic property kills the pathogens and resists the microbial attack. It has ability to generate ROS (reactive oxygen species) by which it can oxidize the cell of the microbes. Copper ion binding and cross linking between genome strands can damage the viral genomic DNA. DNA is a potential target for cytostatic drugs. Cu^{2+} binds to DNA (Fenton type reaction) and generates ROS which leads to the degradation of DNA. Copper can also destroy the microbes by degrading their genomic and plasmid DNA.

Any microbe present on copper surface cannot live much time. Presence of copper ions kills the virus or bacteria. This phenomenon is called "Contact Killing".

Five enveloped or non-enveloped, single or double stranded DNA or RNA viruses are inactivated in presence of Cu(II). Presence of peroxide catalyzes this process. Compared to Fe(II), Cu(II)-peroxide is more effective antimicrobial agent against herpes, T7, Φ×174, Φ6 and Junin simplex viruses. Copper surface is more antimicrobial than stainless steel surface. Copper shows a significant decrease of 83% microbes compared to other metals (Fig. 2).

A Comparison of Antiviral property between Copper and Stainless Steel is shown below:

Type of Surface	Time Period	Microbes Present
Copper Surface	After 6 hours	500
	After 24 hours	_
Stainless Steel Surface	After 6 hours	_
	After 24 hours	500000

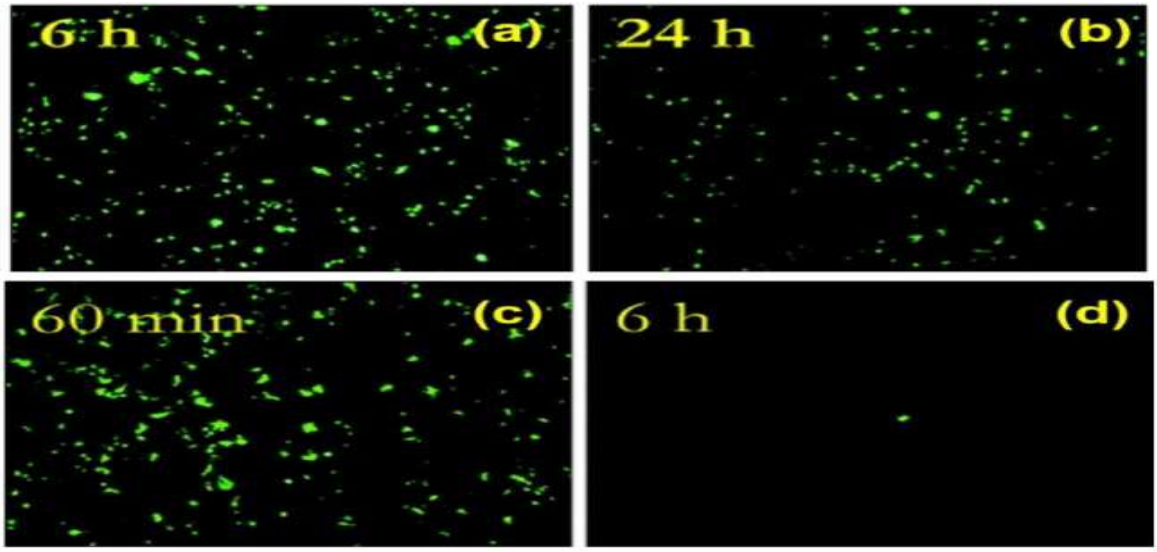

Fig. 2. (a),(b) Influenja virus present on stainless steel surface after 6 and 24 hrs respectively. (c),(d) Influenja virus present on copper surface after 6 and 24 hrs respectively.

The viral genomes were disrupted by copper exposure, and the morphology was irreversibly changed, inducing the disintegration of envelop and dispersal of surface spikes. Inactivation triggered by Cu(I) and Cu(II) aided by ROS generation on alloy surface leading to faster inactivation as compared to non-enveloped viruses. In 'Contact Killing' mechanism (Fig. 3) at first copper enters into the microbial cell and destroy the DNA restricting their metabolism, respiration and reproduction. Again large amount of copper damages the cell-membrane of bacterial cells inducing the loss of cytoplasm. Further generation of ROS destroys the cells.

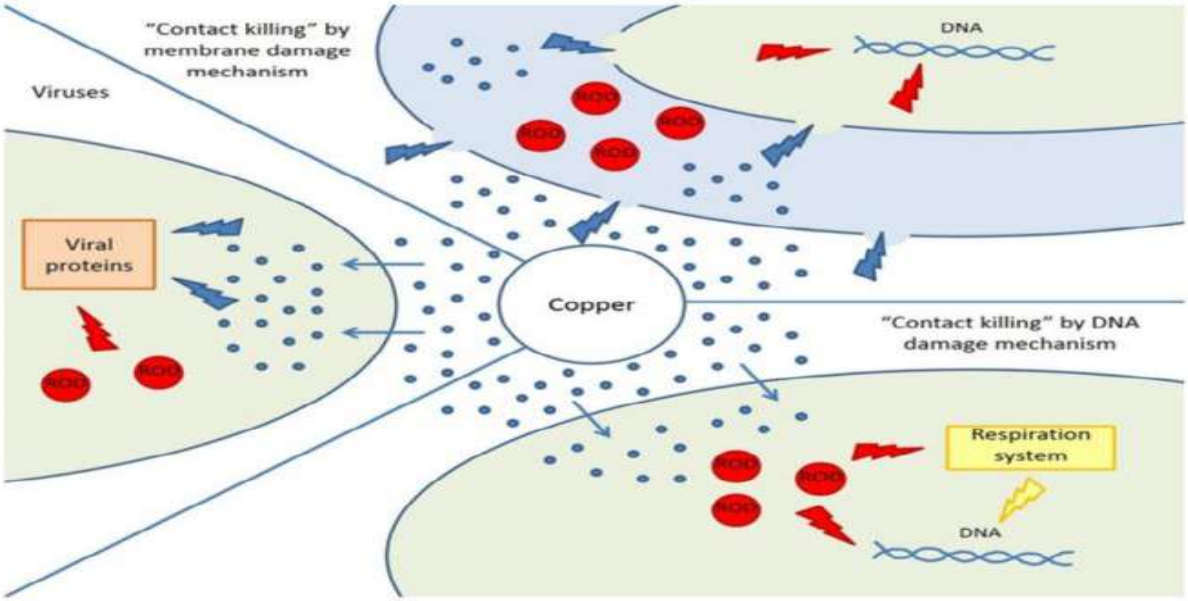

Fig. 3. Contact killing mechanism.

Effectiveness of Copper on COVID-19 compared to other Material

In comparison with other materials, brass alloy with more than 70% copper, exhibit superior virucidal action on HuCoV-229E. There was no trace of viruses on the surface within a short time duration of 60 min whereas on the surface of stainless steel, plastic, PVC, glass and ceramics, there were viruses present even after 5 days (Fig. 4). Virucidal effect is proportional to the copper content of an alloy. On the surface of stainless steel and plastics where SARS-CoV1 and SARS-CoV-2 were present even after 72 hrs, copper surface were clear from them only after 8 hrs and 2 hrs respectively.

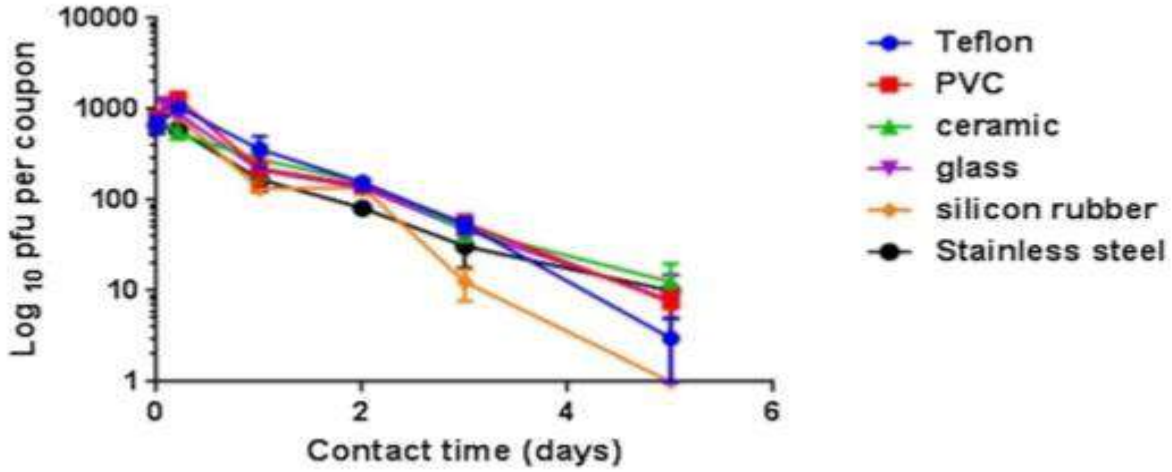

Fig. 4. A comparison on virucidal action of different materials.

Doctors and medical workers always come in contact with viruses. The surgeons and their surgery equipments also have a great chance to come in contact to the viruses. So, to disinfect or sanitize the equipment copper solution is very effective to shield the viral contamination. Copper, due to its rapid inactivation, viral RNA destruction and structural damage, may be used in control of respiratory virus transmission such as MERS and SARS, also used in highly touchable surfaces.

Copper-based materials in fighting COVID-19 Virus

Copper-based materials are daily used as surface disinfectant. Their antiseptic and antifungal effects make them special leading to the production of drugs.

Copper-based Alloys: Recent studies have proved that copper-based alloys have great properties like antiviral, antibacterial and they can be used as virucidal drugs.

Copper alloy affects herpes simplex, bronchitis, HIV-1, hepatitis-C, murine norovirus (MNV-1), poliovirus, 44-monkeypox, covid-19 by damaging biomolecules, RNA, DNA, genomes and protein shell (Fig. 5).

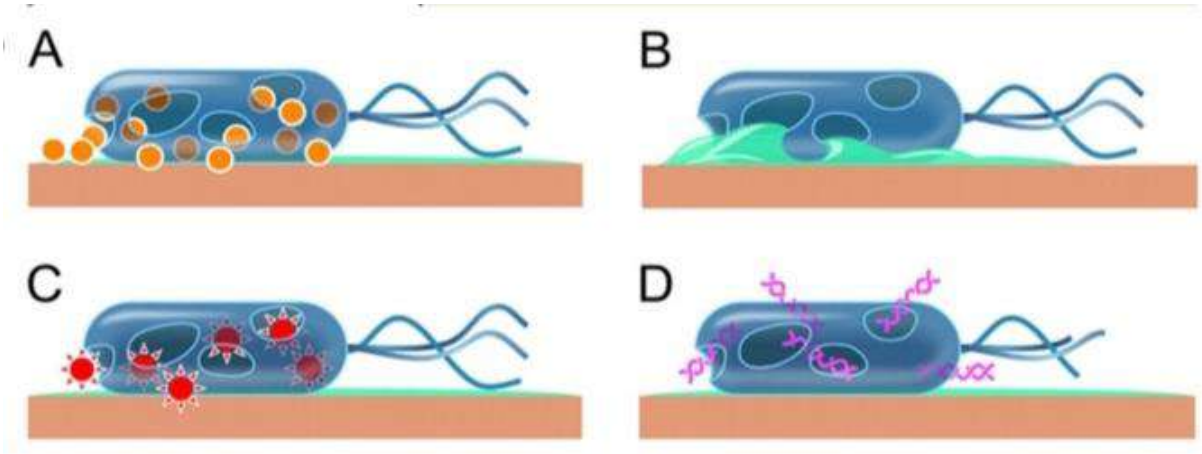

Fig. 5. Illustration of contact killing mechanism on a copper surface (**A**) rupture of cell membrane, (**B**) loss of cytoplasmic content, (**C**) generation of other ROS by copper ions, (**D**) degradation of DNA.

During experiment it is detected that less than 1.1log10 reduction in RNA copy number of HuNoV genome happened in stainless steel surface after a time period of 240 min whereas, 2-3log10 reduction occurred only within 60 min with 70% copper alloy.

Copper bearing stainless steel 316L-Cu SS was favourable as antibacterial substance preventing Implant Related Infection (IRI) both in vitro and in vivo. Copper alloy takes minutes or hours to inactivate viruses depending upon whether the virus is gram-positive or gram-negative, enveloped or non-enveloped. It is also seen that in case of norovirus (MNV) pure copper metal took 30 min to kill the surface-germs and copper alloy took 60 min. This study is temperature dependent.

These values and data are obtained electronic microscope images. Copper-based material, calcined copper (Tamra Bhasma; Ayurveda) is effective on similar microbes. But Tamra Bhasma with and without Amrutikarana did not show any toxicity at low level but shows mild toxicity in liver, kidney, heart, thymus on rats. Copper glass ceramic powder destroys plasmid DNA and RNA. This powder reduce greater than 99.9% bacterial colony.

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Name of the Microbe	Copper Alloy Name	Microbes killed after 12 hrs	Microbes killed after 24 hrs
E. coli	Ti-Cu	96.8%	99%
S. aureaus	Ti-Cu	80%	99%
Anaerobic Polyphyromonusgingivalis	Ti-10 Cu (10% Cu)	_	75%
H1N1	CuFeCrCoNi	_	99.99%

Copper-based Nanoparticles (NPs): Nanoparticles having diameter less than 100 nm have medical properties and used in drug synthesis and therapeutics. The NPs are associated with wide surface area which assist in improving interaction with microbes, affects on a broad spectrum of microbes. Recent studies are improving to induce antimicrobial activity of NPs.

Metal NPs have potential to stop viral replication and propagation causing viral inactivation and virucidal effects by blocking cell-virus attachment and stop the entry of virus into the cells. Thus NPs can be used against many human pathogens like herpes, bronchitis, SARS CoV, polio virus etc. NPs destroy the outer layer of covid-19 virus. Copper based NPs are used as biocidal in wounds dressing and socks. Broad spectrum activity on many enveloped and non-enveloped virus leads to use of copper as antiviral agents, which can induce cytotoxicity in microorganisms. NPs can degrade the capsid protein of norovirus. H1N1 and herpes like viruses are killed by oxides and iodides of NPs.

NPs are used as antifouling agents. CuI-NPs are used in mask, filters etc. Ayurveda describes many antiviral properties of several Ayurvedic Bhasma like Tamra Bhasma (Cu-NP), Rajata Bhasma (Ag-NP), Swarna Bhasma (Au-NP), Lauha Basma (Fe-NP) etc. NPs are used for drug production also. Bacterial colony may be destroyed more by increasing Cu concentration of CuO and CuI NPs. Cu has great affinity towards S and P and so it destroys viral DNA. They penetrate the cell membrane causing membrane damage, loss of cytoplasm and DNA degradation. Ag-Cu alloy prevent HIV replication and E. coli growth.

Copper ions form complexes with biomolecules which causes protein degradation also. Cu-NPs have anti-parasitic and anti-cancer property as well.

Copper-based Coating Technologies: Bulk component materials of copper may be replaced by Cu-based or Cu-coated surface. Cold-spray technique is used to deposit copper on surface like stainless steel surface which exhibit viricidal activity in a short duration of 7 min. Through cold-spray technique making 0.7 mm coating 96% covid-19 virus within 2 hrs and 99.2% covid-19 virus within 4 hrs may be removed (Fig. 6).

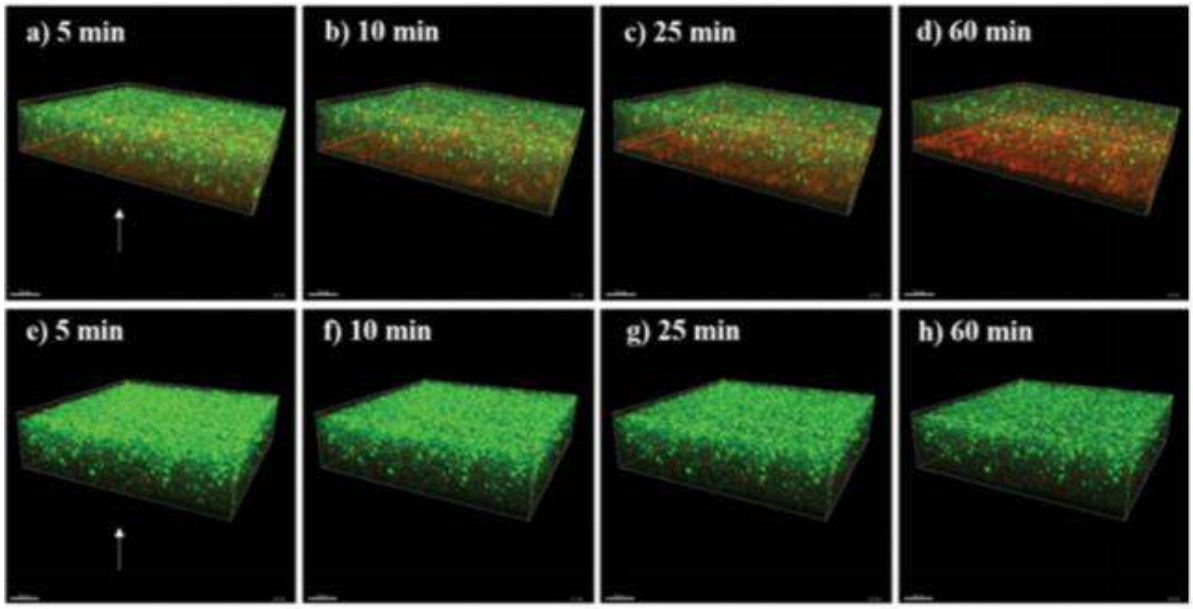

Fig. 6. Increased bactericidal activity as evidenced by the presence of more dead cells (red colour, a – d) on copper – silver alloy coating compared to uncoated stainless steel surfaces with predominant live cells (green colour, e – h).

'Quick and fix' method and 'Thermal spray' method are also used to make copper coated surface. For antibacterial use copper coated plate may be used in daily use surfaces like door push-plate, chair arms, charting tables etc. Various microbes like Pseudomonus, E.coli, Staphylococcus etc. are killed on copper surface. Improved bacterial resistant has been explained to be arising from (Fig. 7):

(a) Bacterial cell oxidation due to galvanic coupling induced redox reaction

(b) Copper ion release and

(c) Localized rise in pH.

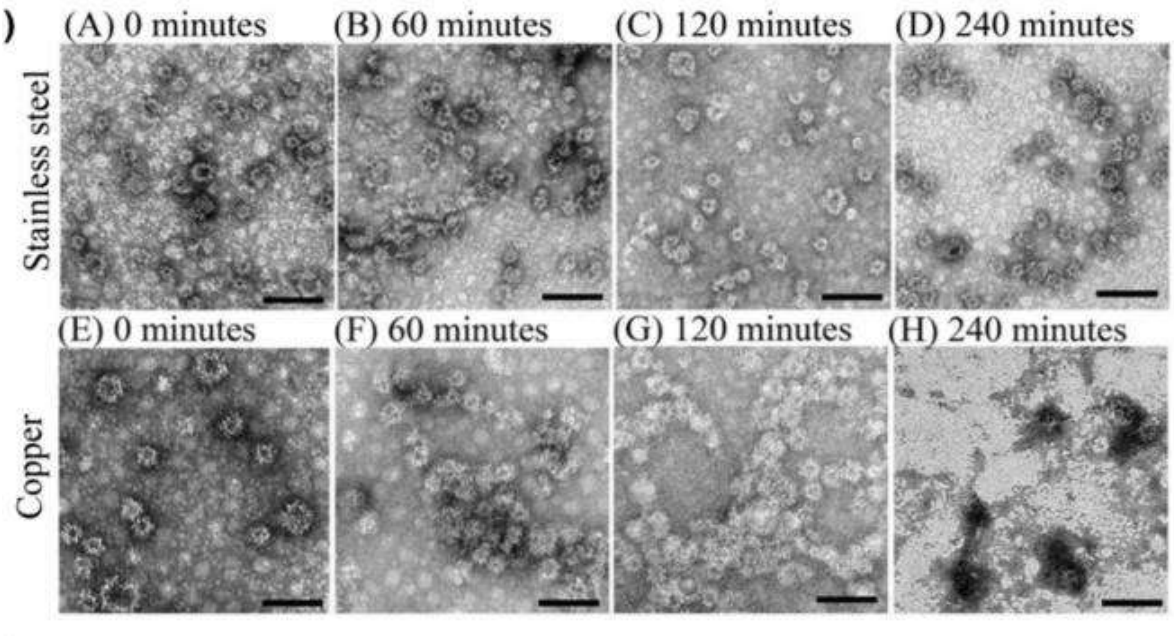

Fig. 7. Virucidal properties of copper and stainless steel.

The developed surfaces show biofilm eradication of gram positive bacteria within short time as compared to slow removal of gram negative bacteria.

For controlling the spread of covid-19 cyta-coat (bio-compatible antibacterial covering) in face mask. Fluidic coating compounds can also be used as antiviral coating material made of nanomaterials with a significant high heat impact. They can form localized hot-spots under light stimulation and destroy viruses or inactivate the spike proteins (Fig. 8).

Fig. 8. Applications of copper.

Limitations of Copper Usage

Inspite of its excellent antiviral properties, copper-based materials have some limitations which need to be taken into account for effective medical applications, copper is essential for humans and deficiency of copper affects health. Since, deficiency and excess of copper can have negative health effects, assessing copper specifications and upper safe limits for intake is difficult. Since copper is expensive and harder to clean without causing corrosion, its widespread use for medical application is limited. On exposure to air, copper undergoes rapid oxidation which in turn limits its antimicrobial use in aerobic condition.

Conclusion

Bacteria, viruses, and other disease-causing microorganisms are more likely to be found in public places like airports, shopping centers, and hospitals. Since the covid-19 virus that is causing the pandemic is so contagious, it is critical to keep the virus from spreading further. The influence of copper can be summarized as follows:

(1) On copper surfaces, the covid-19 virus is active for less than 4 h, compared to plastic and stainless steel on which the virus was present for more than three days.

(2) Therefore, if the contact surfaces are made of copper, the spread of the disease would be minimized. In addition, copper is preferred for door knobs, push plates, handles, stair railings, restroom faucets, and other applications. All of these public surfaces are more prone to spread disease-causing microbes to hands, resulting in infection.

(3) Copper has inherent antimicrobial properties. When cleaned thoroughly and on a regular basis, infectious pathogens can be effectively inactivated on regularly touched surfaces made of uncoated copper alloy materials.

(4) The exposure of copper to COVID-19 has been reported to inactivate viral genomes and showed an irreversible impact on virus morphology, including envelope disintegration and surface spike dispersal.

(5) Since corona viruses are structurally similar, copper alloy’s anti-coronavirus activity is likely to be effective to all coronavirus strains.

Of course, hand washing, good hygiene, and social distancing remain the most successful ways to fight COVID-19 or any such viruses. However, strategic copper usage will

complement these steps, allowing the physical environment to effectively combat harmful bacteria and viruses.

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SITE SELECTIVE CHEMICAL CLEAVAGE OF PEPTIDE BONDS

Project work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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Under the supervision of Dr. Chandrakanta Bandyopadhyay

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Acknowledgements

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SITE SELECTIVE CLEAVAGE OF PEPTIDE BONDS

Abstract

Site-selective cleavage of peptide bonds at serine unit under neutral aqueous conditions is reported. The method relies on the activation of the backbone amide chain at serine residues by the formation of a kinetically favourable five-membered cyclic urethane ring moiety. This activation increases the susceptibility of a peptide bond toward hydrolysis. The method is highly specific and demonstrates broad substrate scope Including cleavage of various bioactive peptides with unnatural amino acid residues, which are unsuitable substrates for enzymatic hydrolysis.

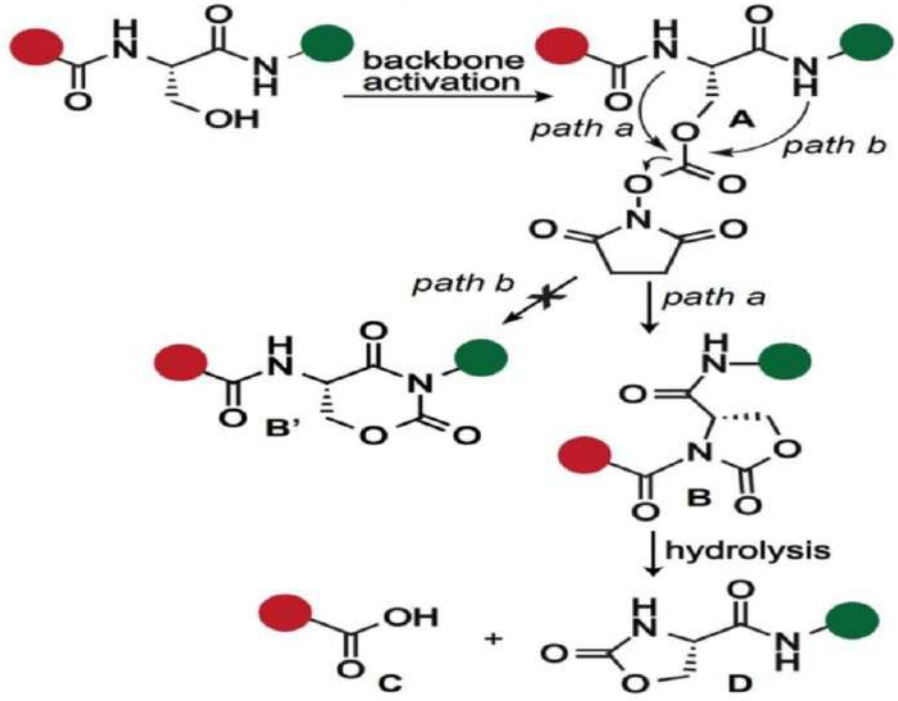
Introduction

Site selective cleavage of peptide bonds at a specific residue is an important biochemical tool for correlating protein structure with activity and various new bioanalytical and bioengineering applications. These new methods require residue-specific cleavage of a peptide bond into large fragments. The peptide Bond (i.e., the amide group), however, is highly stable toward hydrolysis, and the half-life for nonselective cleavage at room temperature and pH 4−8 is 500−1000 years. Few enzymes and synthetic reagents are commonly used for selective hydrolysis of peptide bonds.6 most of these peptidases are ok-selective, Such as trypsin, which is selective for cleavage at Arg and Lys; Chymotrypsin cleaves at Phe, Trp, and Tyr; pepsin at Phe and Leu; The selectivity of peptidases can be adjusted by varying the digestion time and the degree of prior unfolding. Nonetheless, Peptidases are limited because they tend to produce short fragments ill-suited for bioanalytical applications, moreover, these enzymes require narrow ranges of temperature and pH. The existing chemical reagents, such as cyanogen bromide,7 2- Nitro-5-thiocyanobenzoic acid,8 and 2-iodosylbenzoic acid, cleaving peptide bonds often require harsh conditions. As a result, side reactions and the lack of specificity of amide-bond hydrolysis limits their scope in chemical biology and synthetic application. Recently, asparagine-selective cleavage of peptide bonds by using diacetoxyiodobenzene has been reported. Use of metals for cleavage of peptide bonds has been intensively studied, but their practical use for protein analysis is still in its early stages. Applications for controlled and

specific cleavage, a daunting task, a chemical reagent must selectively bind only to one particular amino acid in the peptide sequence and specifically cleave the peptide bond at the binding site.

RESULTS & DISCUSSION / SUMMARY OF THE WORK

Chemical methodology that selectively cleaves the peptide bond at serine residues with high efficiency. Selective cleavage was achieved by chemical modification of the amide backbone chain to the cyclic urethane moiety (B), Scheme(1) which has very susceptible to hydrolysis under neutral, aqueous conditions. Most importantly, the reactive side chains of amino acid remained unmodified under the reaction conditions, preferred over existing cleavage methods which yield irreversibly modified fragments. The serine-selective cleavage of peptide bonds by the reaction of their side chain hydroxymethyl group with N,N'-Disuccinimidyl carbonate (DSC) to generate an activated of the amide nitrogen of the peptide backbone on intermediate(A) could produce a five-membered cyclic urethane ring (B) through path a six-membered ring (B') by following path b (Scheme 1). Our studies suggest the high specificity for the formation of the kinetically favourable five-membered cyclic urethane ring (B), of the peptide bond at the cyclic urethane moiety (B) produces an N-terminal peptide fragment (C) and many NMR ,IR, Mass



Scheme 1. Rationale for the serine-selective modification and peptide bond cleavage in neutral aqueous solution.

spectrometry is done and results that modified C-terminal fragment can undergo ring opening under basic conditions reverting back to unmodified serine at the terminus with the original fragment in hand, it is possible to proceed with semi-synthesis by further coupling with another peptide or protein. To determine the effect of the side chain functionality of the preceding serine on the cyclization and cleavage of the peptides, various hexapeptide, Fmoc-Gly-Xaa-Ser-Phe-Ala-Gly with different residue at the Xaa position .Thus, after incubation in buffer (pH 7.5) for some hours C-terminal fragment Oxd-Phe-Ala-Gly was obtained in all the cases with varying HPLC conversion(70- >99%).The results indicate that peptides with Xaa =Gly, Met , His , Tyr,Trp , and Asp underwent smooth conversion to cleavage products after 48 hr similar to Xaa = Ala. This occurs in contrast to known chemical reagents, which result in over-oxidation in Tyr,Trp, and Met containing peptides. The peptide with a bulky amino acid adjacent to serine, (Xaa = Val), gave moderate yield after four days in phosphate buffer (pH 7.8) Peptide 1h (Xaa= Lys) with a free side chain amine, also reacted with DSC and upon treatment with buffer underwent desired cleavage at the Lys-Ser bond and generated the N-Terminal carboxylate lysine derivative and the C-terminal fragment, Oxd-Phe-Ala-Gly, n-terminal carboxylate lysine derivative 3h eventually underwent decarboxylation to generate N-terminal fragment, Fmoc-Gly-Lys-OH . In the case of peptide with a Pro residue next to serine, easy cyclization and cleavage at the Pro-Ser bond was observed, which is in contrast to enzymatic degradation, where Pro at a subsequent position nearly blocks the cleavage completely independent the substrate scope of this reaction was further evaluated The reaction was also applicable to substrates containing threonine . After treatment with cleavage was observed at the N-terminal side of both serine and threonine, which is expected due to the similar side group functionality exhibited by both residues. Peptide , Threonine side chain cyclization required a higher amount of DSC than the cyclization at serine residue .Peptides with multiple serine residues gave comparable results (75-79%). Peptides, which contain D-amino acid residues and are unsuitable for various enzymatic degradation, were successfully cleaved under the reaction conditions . In comprising an intramolecular disulfide bridge, afforded the cleavage product at the Ser with intact disulfide bond. This methodology allows for determination of disulfide pairing positions in a peptide chain, which is in contrast to other chemical reagents. As expected, peptide Fmoc-Gly-Ala-Cys- Phe-Arg-Phe-Gly-NH2 with a free cysteine residue underwent cleavage at the N-terminus of cysteine and generated a thiazolidinone modified C-terminal fragment Thz-Phe-Arg-Phe-Gly-NH2 and the N-terminal fragment Fmoc-Gly-Ala-OH Surprisingly, peptide

Surprisingly, the peptide containing Glu along with a unit of serine underwent cleavage at the N-terminal of both Glu and Ser to generate three which are fragments under the reaction conditions . Activation of Glu by DSC for scission takes place by the formation of a five membered pyroglutamyl imide moiety (pGlu) recently, we have reported the site-specific activation of glutamic acid for hydrolysis of a peptide bond by using PyBro The cyclization of Glu under reaction conditions occurs in contrast to the peptide containing Asp which also has a free carboxylic acid side chain but cleavage was observed only at serine residue . Next, to demonstrate the compatibility of this methodology with a free main chain carboxylic group, a peptide Fmoc Gly-Ser-Gly-Phe-OH was synthesized on wang resin.26 under the reaction conditions, cleavage was observed only at the N-terminus of serine containing Glu along with serine underwent cleavage at the N-terminal of both Glu and Ser to generate three fragment under the , The activation of Glu by DSC for scission takes place by the formation of a five membered pyroglutamyl imide moiety (pGlu) .Recently, we have reported the site-specific activation of glutamic acid for hydrolysis of a peptide bond by using Pybrop the cyclization Glu under reaction conditions occurs in contrast to the peptide containing Asp which also has a free carboxylic acid side chain but cleavage was observed only at serine residue . Next, to demonstrate the compatibility of this methodology with a free main chain carboxylic group, a peptide Fmoc Gly-Ser-Gly-Phe-OH was synthesized on Wang resin.26 under the reaction conditions, cleavage was observed only at the N-terminus of serine residue.

Conclusion

Site-selective hydrolysis of unreactive peptide bonds under mild and metal-free reaction conditions has been developed. The methodology utilizes the activation of a backbone amide chain to cleave the peptide bond specifically at glutamic acid. The chemical reagents can be easily removed after the cleavage, unlike proteases. Disulfide bonds are stable toward the reaction conditions; thus, this methodology can be used to determine the position of disulfide pairing in peptides. This method exhibits broad substrate scope, including the cleavage of peptides at the Pro-Glu site, as such kind of site is resistant to enzymatic degradation. Since the hydrolysis of mutated peptides with unnatural amino acid residues such as D-amino acid, which are unsuitable substrates for enzymes, proceeded with ease under the reaction conditions, this methodology can be used to determine the mutations responsible for various diseases. This technology is highly specific for hydrolysis of peptides at one particular

residue, which is one of the key requirements for semi synthesis and bioengineering of fusion proteins. These studies lay the groundwork for further studies aimed at developing artificial chemical proteases for the cleavage of target proteins responsible for various diseases and exploring this reaction for biotechno-logical applications.

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SITE SELECTIVE PEPTIDE CLEAVAGE

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

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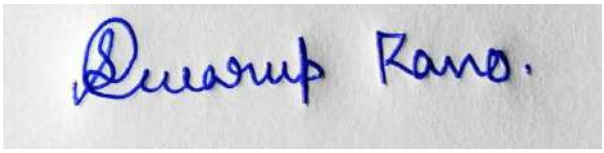

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SITE SELECTIVE PEPTIDE CLEAVAGE

ABSTRACT:

Generally amide bonds of peptides and proteins are unreactive towards hydrolysis. Chemical cleavage methods enabling site-selective peptide/protein degradation is an essential moderation of biologically relevant macromolecules which compliments enzymatic hydrolysis. It is a very important chemical modification that provides invaluable information regarding protein sequence, and it acts as a modulator of protein structure and functions for therapeutic applications. Now science community has developed various methods for site selective peptide cleavage such as metal-promoted peptide hydrolysis,hydrazinolysis, oxidative peptide bond cleavage, using non-metal oxidant, through side chain modification etc. In this review the recent progress in chemical, site-selective peptide bond cleavage is evaluated with an importance on postulated mechanisms and their implications on reactivity , selectivity , and substrate scope.

INTRODUCTION:

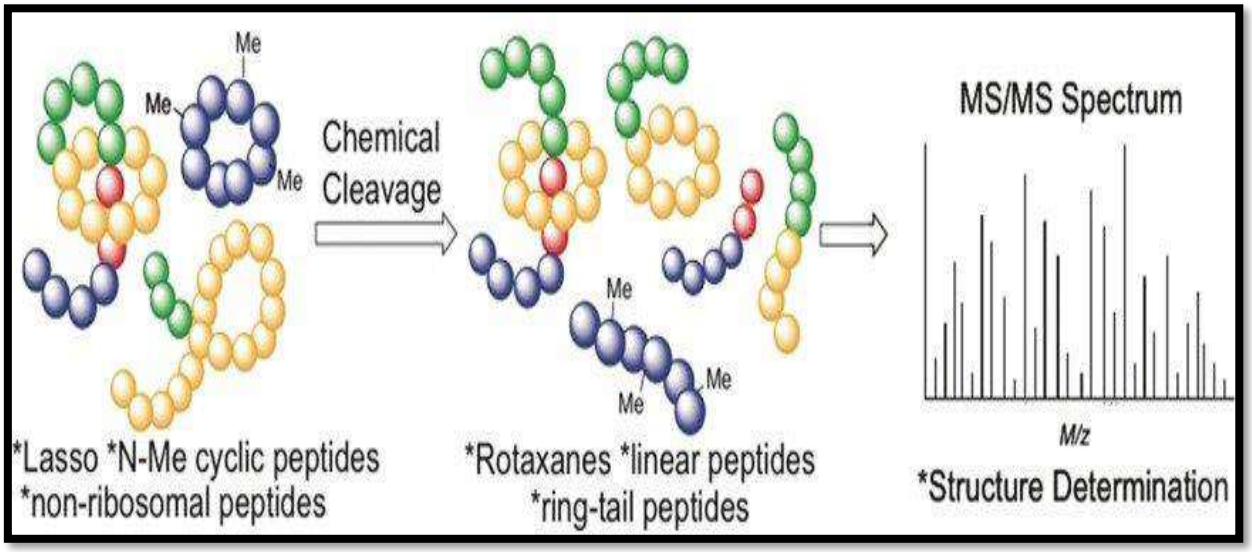
Site selective cleavage of peptide bond is a very importantchemical modification which is used for protein designing and has various applications in bio-analytical, bio-therapeutic, and protein engineering techniques. For the selective hydrolysis of peptide bond, enzymatic cleavage is commonly used. Proteases are commonly used in protein hydrolysis include: trypsin (cleaves at Arg and Lys), chymotrypsin (Phe, Trp and Tyr), and pepsin (Phe and Leu). While proteases cleave protein with high specificity, they have several disadvantages. They are sometimes limited because they contaminate the protein digests and they requires narrow ranges of temperatures and pH for optimal activity. Moreover proteases often have high site-selectivity that can limit their use for proteins containing unnatural residues and post translational modifications. Therefore chemical cleavage methods have been developed as complementary approaches to enzymes due to their applicability to a wide range of substrates.

Amide bonds exist in peptide and protein structures and therefore recognised as one of the most fundamental and important chemical bonds in nature. Delocalization of the lone pair electrons on the nitrogen atom over the amide functionality makes the amide bond stable. 350-600years is the estimated half-life of amide bonds in spontaneous hydrolysis in a neutral

pH solution at room temperature. Harsh reaction conditions are required for amide hydrolysis in traditional methods such as strong acids or bases at high temparature . In a broad range of research fields protein modifications through chemical method are of a great importance for example chemical biology, chemical genetics, protein-engineering, proteomics and drug discovery.One of the valuable chemical tools among important chemical modifications is the site-specific peptide bond cleavage reaction.One of the valuable chemical tools among important chemical modifications is the site-specific peptide bond cleavage reaction.For example structural determination of peptides and proteins in proteomics, chemical biology and structural biology studies are some of them.

Inspite enzymatic (peptidase) hydrolysis of peptide bonds proceed at certain sites under mild conditions with high fidelity, in principle to genetically encoded amino acid sequence the scope of the scissile substances are restricted.In substrates containing unnatural or structurally modified amino acids chemical methods are applied which are not recognised by pepidases. Therefore it is challenging that the development of artificial peptidase enabling practical and general protein/peptide cleavage,but of noteworthy utility in a variety of applications ranging from structure determination of chemically modified proteins/peptides to therapeutics.

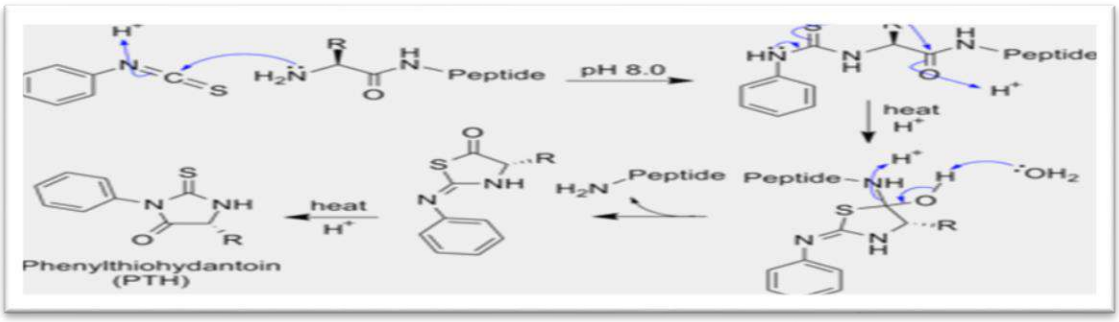
In this chapter, we will take a look at the current past (during last 75 years) advancement in site selective peptide/protein degradation through chemical cleavage methods that complement enzymatic hydrolysis.



RESULTS & DISCUSSION:

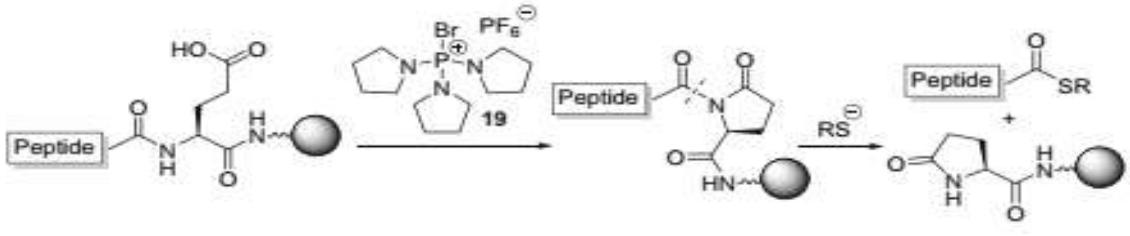
Site-Specific Peptide Cleavage bySide ChainModification:-

Edman degradation, developed by PehrEdman is a method of sequencing amino acids in a peptide. In this method, the amino-terminal residue is selected and cleaved from the peptide without disrupting the peptide bonds between other amino acid residues. Firstly it's postulated that the ease of reaction parallel ease of ring closure to hydrantoin and from that we can prefer the use of phenylthiocarbamyl derivatives. Secondly the cleavage should be take place exclusively of the peptide bond adjacent to the carbamyl group without changing the configuration of the other bonds. Since water is not required for the hydrantoin synthesis whereas the peptide bonds are cleaved by hydrolysis or analogous reaction and the reaction is carried out in an anhydrous, inert solvent nitromethane. In presence of nitromethane saturated with hydrogen chloride the phenylthiocarbamyl dipeptide is cleaved into phenyl thiohydrantoin and amino acid at room temperature.



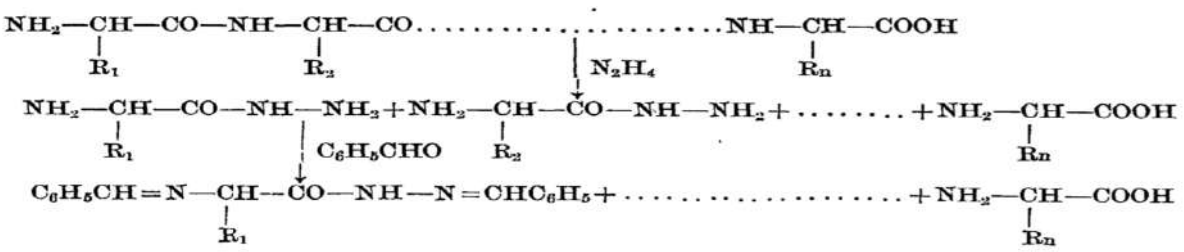
Cysand Met are among the most studied cleavage sites because of the high nucleophilicity of sulfur atoms.

In 2012, Kajihara and Okamoto reported a method for cleavage of N-terminus side peptide bond of Cys residue and generation of thioester using [PhOC(S)Cl].In Jensen's work the similar type of concept is found. The key step involves activation of carboxy group of a Glu side chain by PyBrOP and this results the formation of pyroglutamyl moiety. The process as follows-

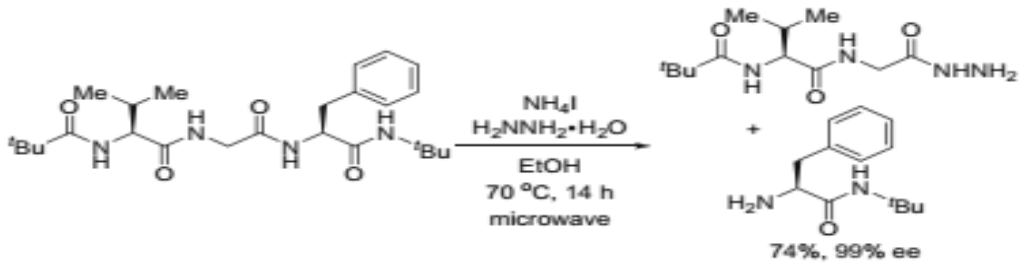


Hydrazinolysis :-

In 1952, ShiroAkabori and his co-workers have investigated hydrazinolysis of peptide backbone of protein for the purpose of finding a simple method of the characterization of carboxyl-terminal amino acids in protein. When protein is treated with anhydrous hydrazine under certain condition, only carboxyl terminal amino acids are obtained as a free amino acid and other amino acids are converted into the amino acid hydrazides. The process is given below-



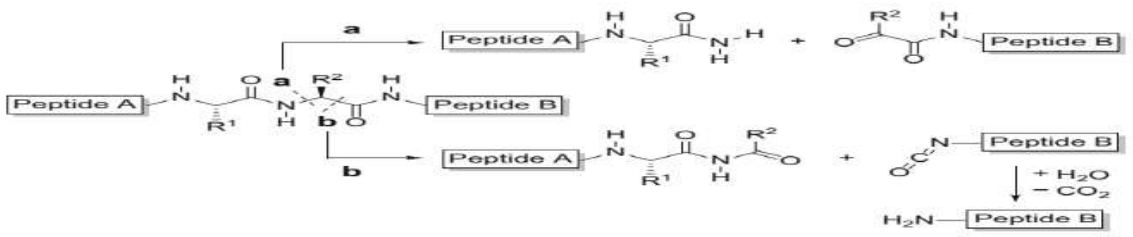
In 2012, Ohshima and co-workers have published their report about microwave-assisted transamidativedeacylation of unactivated amides with the help of ammonium salt and ethylene diamine at the temperature of 50-90^{o}c. In 2014 the same group reported the hydrazinolysis of unactivated amide bonds at 50-70^{o}c to provide *N*-acylhydrazine and amides in good yield. They applied the following reaction condition-



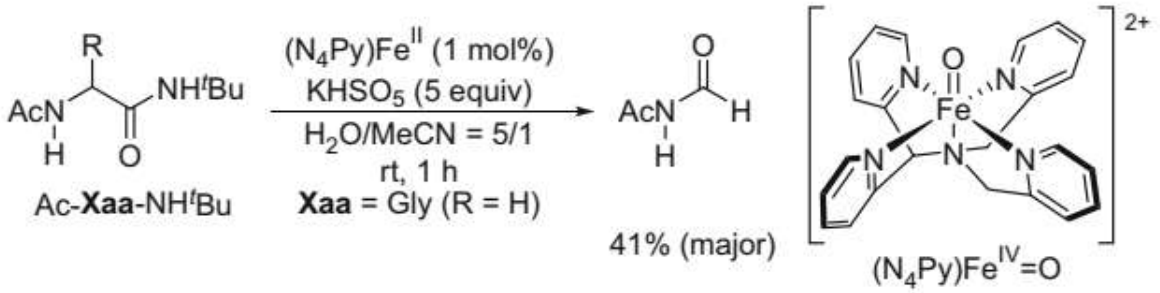
Oxidative Cleavage Assisted by Metal Ions/MetalComplexes :-

The oxidative cleavage can be classified into two types:a)hydroxylation at the α-carbon (Cα) followed by cleavage of the Cα–N bond and b)oxidative cleavage of the Cα–C(O) bond.

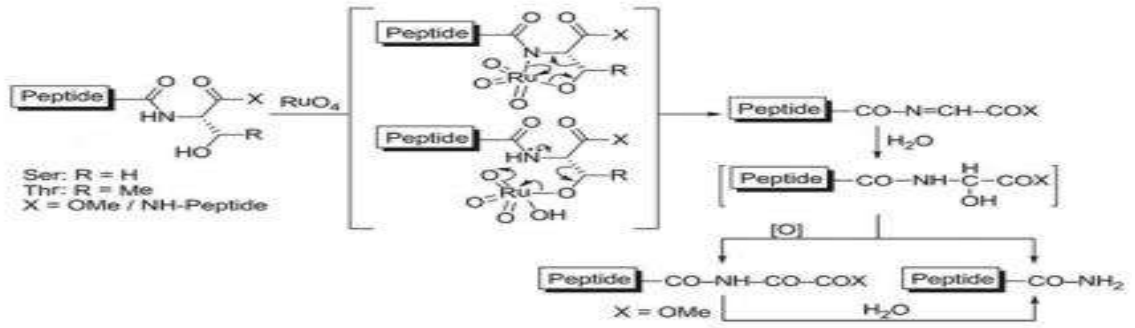
In 2004, QUE reported a non-hemeiron(IV)–oxo complex, $[(N_4Py)Fe=O]^{2+}$did a



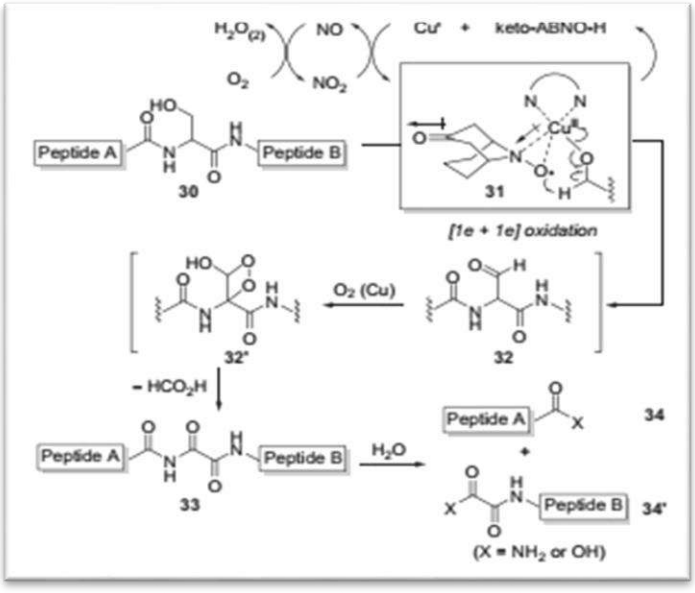
oxidative cleavage in aliphatic C-H bond of cyclohexane molecule at room temperature.In 2007 Kodanko reported a oxidative cleavage of amide of protected amino acids using a iron metal catalyst $[Fe(N_4Py)(MeCN)](ClO_4)_2$ in presence of $KHSO_5$ (oxidant).Oxidation of Ac-Xaa-NH^{t}Bu, takes place where Xaa=Gly, produced *N*-acetylformamide as a major product through Cα–C(O) cleavage.



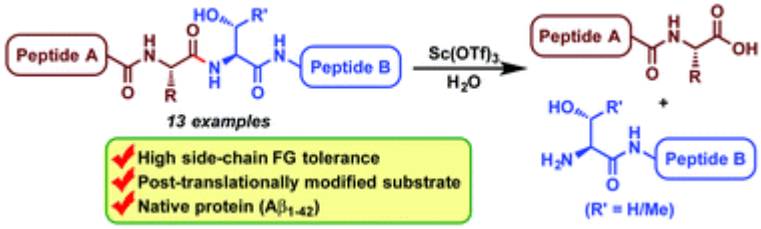
Ranganathan reported catalytic peptide cleavage at serine and threonine through $RuCl_3/NaIO_4$oxidation by generating Ru-oxo complexes as an intermediate.



Recently Kanai and Oisaki reported catalytic aerobic oxidation of amine using combination of a Cu complex and a redox mediator keto-ABNO. In 2014 the same group reported Ser-selective cleavage in aerobic condition using stoichiometric amount of water soluble Cu-complex. Most probable mechanism is depicted here ---



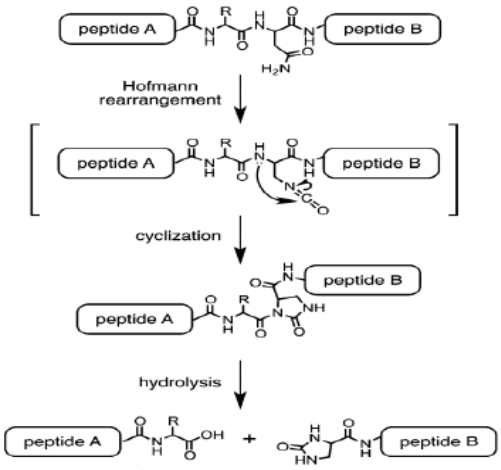
Most recently at *2017, Jizhi Ni, YouheiSohma and MotomuKanai* reported site-selective hydrolysis of peptide bonds at the Ser and Thr positions with a high yield. This chemical cleavage occurs through Sc(III)-promoted N,O-acyl rearrangement and subsequent hydrolysis. The system was further extended to site-selective cleavage of a native protein, *Aβ1–42*, which is closely related to the onset of *Alzheimer's disease*.

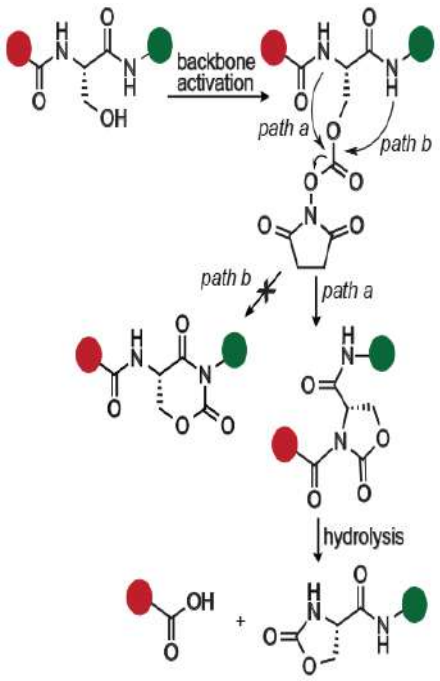


Peptide Cleavage with Non-Metal Oxidant :-

At 1967 E. Gross and Witkop reported that cyanogens bromide is capable of cleaving thioesters. The action of cyanogen bromide upon proteins is unique in its selective attack on methionine. They showed that the reaction between cyanogen bromide and methionine occurred in very mild condition. At 1970,A. Patchornik, Y. Degani and HavaNewmann reported that cysteine peptide bonds can be cleaved *via* a β-elimination reaction of S-dinitrophenylcysteine derivative to dehydroalanine residue. Peptides containing cysteine residues were quantitatively S-cyanylated using the reagent 2-Nitro-5-thiocyanobenzoic acid (NTCB) in dilute solution. W. C Mohany, P. K Smith and M.A Hermodson reported an article in the year 1981. They depicted that *o*-iodoxybenzoic acid, a disproportionation product of O-iodosobenzoic acid, has been identified as a contaminant in most preparations of *o*-iodobenzoic acid capable of both modifying and cleaving certain tyrosyl residue.

In 2014, Kanai and Sohma developed a mild method using diacetoxyiodobenzene(DIB) in aqueous neutral solution at 37ºC for preparing Asp selective peptide bond cleavage. Oxidation of the primary amide group of an Asparagine side chain was the initial step of the transformation, the corresponding isocyanate was prepared through Hofmann rearrangement. The Intramolecularnucleophilic attack of the amide N atom of the peptide bond results the formation of five membered acylurea.

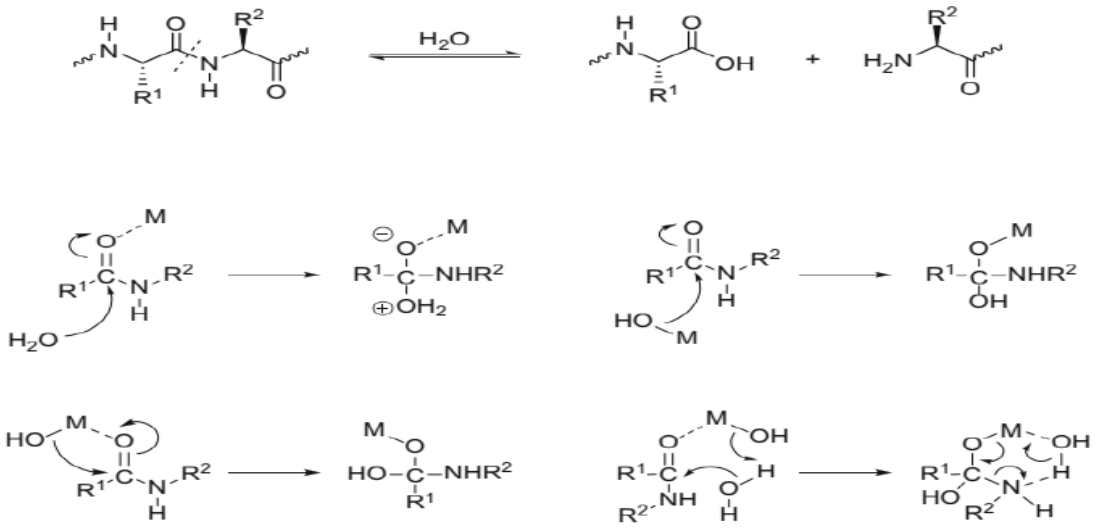




In 2016, Hader E. Elashal and Monika Raj reported serine selective cleavage of peptide bonds by the reaction of their side chain hydroxymethyl group with *N*,*N*-disuccinimidyl carbonate (DSC) to generate an activated intermediate. Intramolecular nucleophile of the amide nitrogen of the peptide backbone on intermediate could produce a five membered cyclic urethane ring through path a or a six membered ring by following path b. Formation of five membered urethane ring is kinetically favoured.

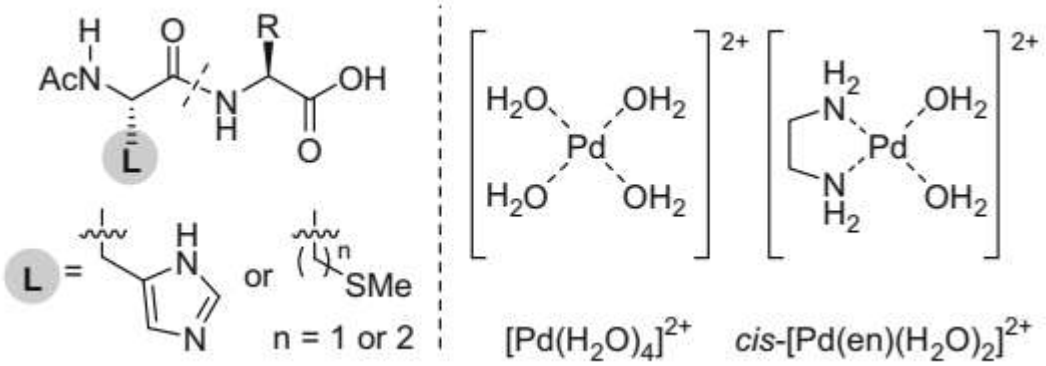
Using Interaction Between Metal Ions and Specific Side Chain Functional Groups of Peptides:

In metal prompted peptide bond hydrolysis,three representative roles of a metal are possible.First, Lewis acidic behaviour of metal to facilitate the nucleophilic attack of hydroxide ions or water molecules on carbonyl groups; second, generation of metal hydroxides for enhancing the nucleophilicity of water molecule as a Bronsted base and third, activation of carbonyl carbon.

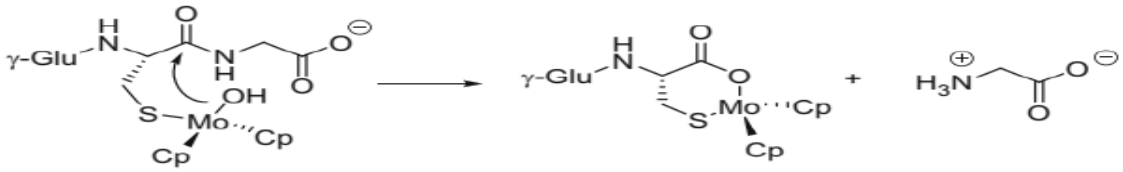


Using $[Pd(H_2O)_4]^{2+}$, cis-$[Pd(en)(H_2O)_2]^{2+}$ and other pd(II) complexes as catalysts,we can cleave various polypeptides and proteins containing co-ordinating residues.(e.g:-S-methyl cysteine). The interaction between nitrogen or sulphur atom of a polypeptide chain with pd(II)decides site selectivity of cleavage.

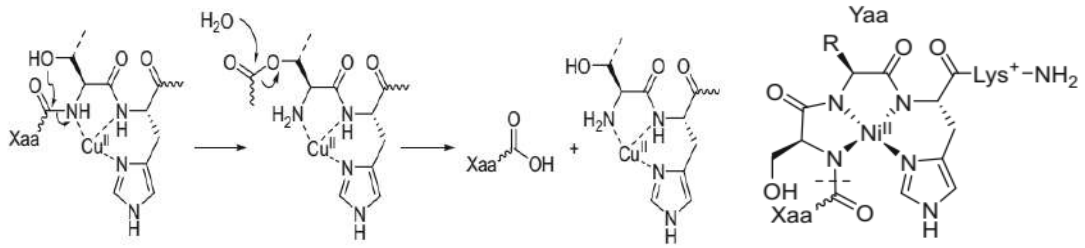
Using *Cis*-$[Pt(en)(H_2O)_2]^{2+}$,the cleavage siteis differed from that using *Cis* $[Pd(en)_2(H_2O)_2]^{2+}$. In case of Pt(II), C- terminal side peptide bond of the anchoring residue is cleaved. The site selectivity for Pt and Pd mainly arises due to the stability of (metal-en) complex.



With the help of chloride / thiolate ligand exchange, the complexCp_2MoCl_2 bounded with the thiol group of cysteine and regioselective hydrolysis of the Cys-Xaa peptide bond in dipeptides and tripeptides by intramocular metal hydroxide (MO-OH) transfer.



For Cu(II) and Ni(II)ions, we can use imidazole group of histidine residue as a very good ligand.In a sequence of Xaa-Ser-Yaa-His-Lys, the Xaa-Ser bond is cleaved using Ni ions at 37^oC and PH 7.4.A stable complex between square planar Ni(II)ions and the Ser-Yaa-His-Lys sequence is formed as a result of cleavage.



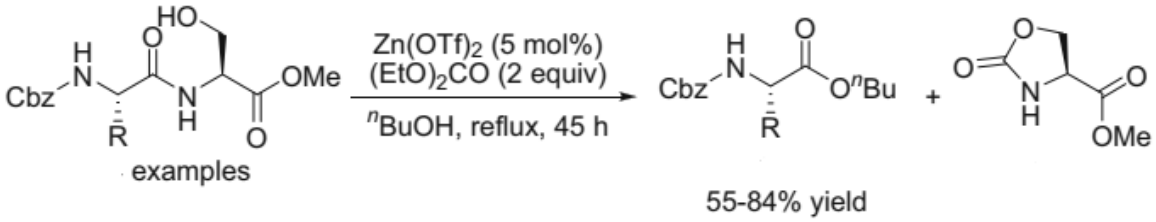
For the promotion of peptide hydrolysis, Zn^{2+} ion exhibits several properties. First, due to complete d-orbital, there is no gain in ligand field stabilisation energy during the co-ordination with ligand in any geometry. Second, according to Hard–Soft Acid-Base principle

,Zn^{2+} behaves as aborderline. As a result a strong interaction with variety of ligand is observed including a sulphur atom of cysteine(Cys), N-atom of His and O-atom of Glu, Asp and water. Third, for facile catalyst turnover, ligand ion exchange on Zn (II) becomes very fast. Fourth, oxidation state of Zn (II) is stable and thus oxidative side reactions are not considered. With these advantages we can found Zn^{+2} as co-factors in the active side of proteases.

In 1961, Gly-Leu was cleaved by treatment with stoichiometric Zn(II) for 24hours at pH 8.6 and 70^{o}C . In 2003, Yashino presented hydrolysis of dipeptides in the presence of stoichiometric $ZnCl_2$ at pH 7.0.

By promoting N-acyl to O-acyl rearrangement, hydrolysis of Ser or Thrwas accomplished.In Xaa-Ser sequences(eg:-Gly-Ser)intramolecular attack of side chain hydroxyl group to the amide carbon undergoes through favourable five-membered ring formation . In case of Ser(Ser)-Xaa sequences (e.g:-Ser-Gly), yield of hydrolysis is very low due to formation of an unfavourable four membered ring.

First Zn-catalysed peptide cleavage was reported in 2012, by Mashima and Co- workers and they reported that $Zn(OTf)_2$ acted as a catalyst for Ser-selective cleavage of peptide.A little amount of peptide cleavage product is obtained from Cbz-Gly-Gly-OMe when we replace the Ser residue with a Gly residue.



Conclusion :-

Methods for site selective chemical cleavage of peptides and proteins have significantly progressed in the last few years. For hydrolytic and oxidative cleavage of peptide bonds metal complexes with high catalyst turnover, especially those containing Zn(II) , Co (III) and Fe (IV), have been rotationally designed and synthesized. Meanwhile site selective peptide cleavage methods under metal free conditions using reactivity of side chain functional group are also proved to be useful for thioester formation toward chemical ligation and for structural determination of unnatural amino acids containing peptides. Despite the fact that significant progress has been made, the abilities of peptide cleavage methods are still far behind natural peptidases regarding catalyst activity cleavage site-fidelity, and substrate

specificity. Research is on progress to fill those gaps. New biology and medicine can be unfolded by the advancement of truly useful and practical artificial peptidases that can complement enzymes. Fundamental chemical breakthroughs are required to do so.

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A REVIEW

ON

SYNTHESIS AND CATALYTIC ACTIVITY OF PALLADIUM NANOPARTICLES

Project Work Submitted for Partial Fulfilment of the B.Sc. (Honours) Degree in Chemistry BY

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Registration Number: A01-1152-112-034-2019 of 2019-2020

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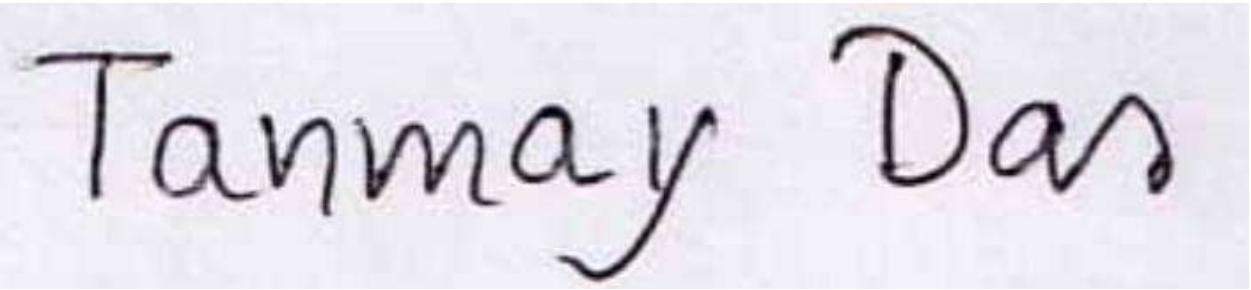

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Date: 15/01/2022

Place: Sagar, South-24-Parganas.

SYNTHESIS AND CATALYTIC ACTIVITY OF PALLADIUM NANOPARTICLES

Abstract :

This project deals with synthesis and catalytic activity of palladium nanoparticles. The PdNPs are synthesized by a simple in-situ method treating a solution of [Pd(OAc)2] with aqueous leaf extract of the plant G.pedunculanta-Roxb in presence of 0.3 mol %of starch. Here also discuss the synthesis and catalytic evaluation of palladium nanoparticles using xanthum gum, acting as both reducing and stabilizing agent without using any synthetic reagent. In room temperature, dyhydrogen is generated from formic acid using synthesized PdxAg1-x nanoporous nanoalloys along with pure PdNPs. Dyhydrogen also generated from hydrous hydrazine under alkali and ambient reaction conditions using bimetallic Ni60Pd40 nanocatalyst with large surface area.

Introduction

Nanotechnology represents one of the major break throughs of modern science, enabling materials of distinctive size, structure and composition to be formed. Such nanodimensional materials(in the 1-100 nm size domain) are seen as a bridge between atomic and bulk materials and have been shown to exhibit a variety of unique chemical, physical and electronic properties[7]. The study of these properties has become an increasingly important area in chemistry, physics, biology, medicine and material sciences. However, reliable preparations of the nanomaterials are required for their exploitation and this remains an area of active research.

Whilst much research has focussed on nanomaterials of the coinage metals(especially those of gold[8],interest in the properties of other transition metal nanomaterials is also considerable and growing[9]. The high surface area to volume ratio makes nanomaterials highly desirable for use as potential catalysts. Given that palladium is one of the most efficient metals in catalysis[10,11] the study of palladium-based materials is hugely important and valuable. As a consequences, nanoparticles of palladium have been heavily studied in a wide range of catalytic applications including hydrogenation [12,13],oxidation [14,15],carbon-carbon bond formation [16,17],and electrochemical reactions in fuel cells[18]. However it should be noted that the applications of palladium go beyond catalysis : For example, the propensity of palladium to

adsorb hydroges has also led to palladium nanoparticles being utilised in hydrogen storage[19,20] and sensing applications[21,22]

Resuts and Discussion

Synthesis :

The PdNPs are synthesized by simple in-situ method treating a solution of [Pd(OAc)2] with aqueous leaf extract of the plant G.pedunculanta-Roxb in presence of 0.3 mol % of starch. Since, we have not used any external reducing agent; it is logical to assume that the phytochemical constituents performed the reduction Pd(II) to Pd(0). In order investigate the photo-constituents responsible for this reduction, we have performed HPLC analysis of the leaf extract and galic acid was further confirmed by HRMS analysis which shows a molecular ion peak [M-2H+] atm/e 168. It believes that in our case also. Here galic acid act as a bio-reducing agent[1]

Solution were prepared with double distilled water. 0.0356 g of PdCl2 was accurately weighed and dissolved in 100 ml of HCl (0.000413M) to form an H2PdCl4 aqueous solution. An aliquot of 5 ml of the aqueous H2PdCl4 solution was mixed with 5 ml of a 2% aqueous solution of XG in a boiling tube. This reaction is carried out in autoclave at a pressure of 15 Psi and at 120 C temperature by 10 minute time[23].

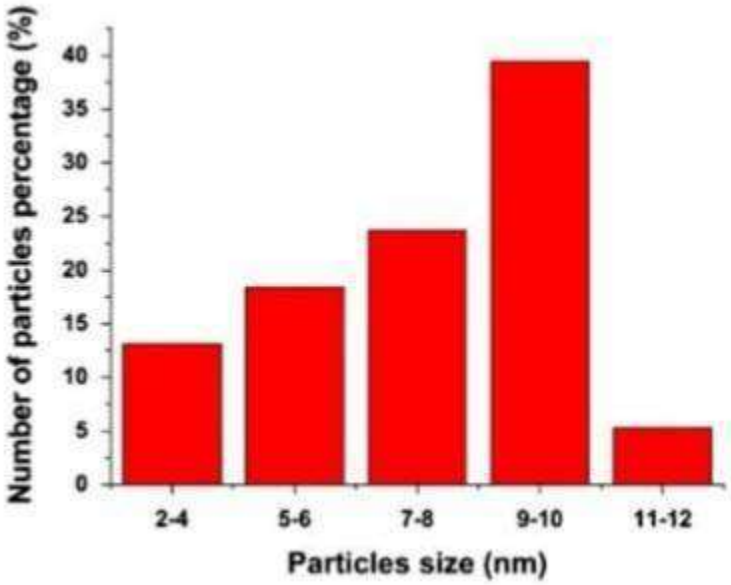
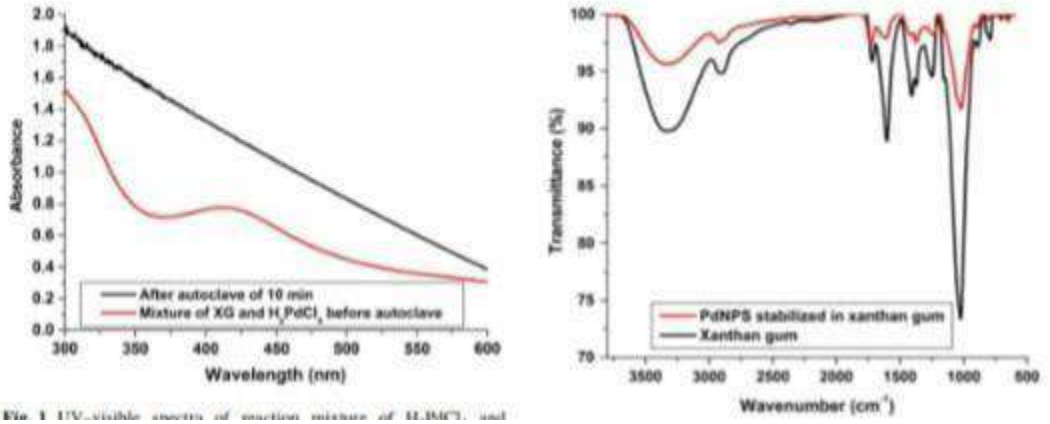


Figure-7



The synthesis of palladium nanoparticles (PdNPs) using an aqueous extract of leaves of Euphorbia thymifolia [3] and their application in the ligand-free stille and Hiyama cross coupling reaction are reported here. PdNPs were characterized using powder XRD, TEM, FT-IR and UV-vis techniques. The synthesized PdNPs exhibited excellent catalytic activity and the reactions generated the corresponding products in good to excellent yields. These methods have some advantage such as efficiency, generality high yield, elimination ligand, organometallic solvent and homogeneous catalyst, cleaner reaction profiles, ease product isolation and simplicity. The reactions were carried out in a green solvent i.e. water. The catalyst was quantitatively recovered and reused without significant loss in the catalytic activity.

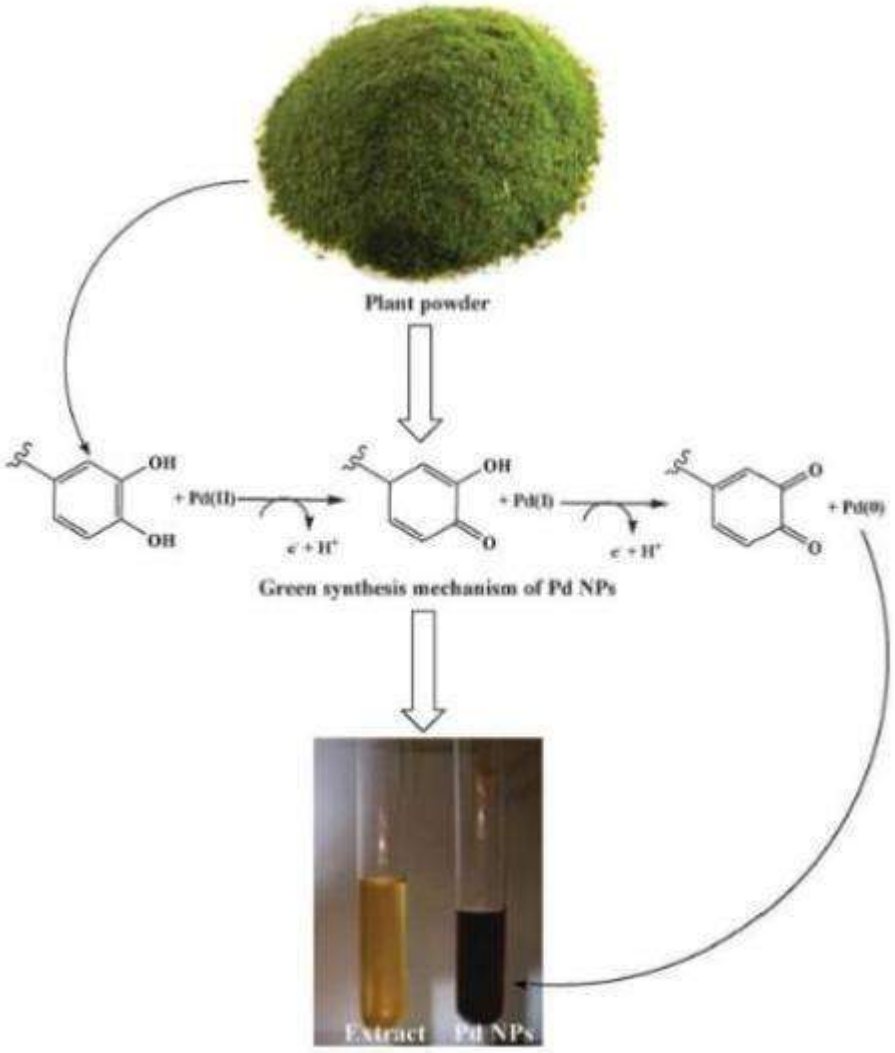
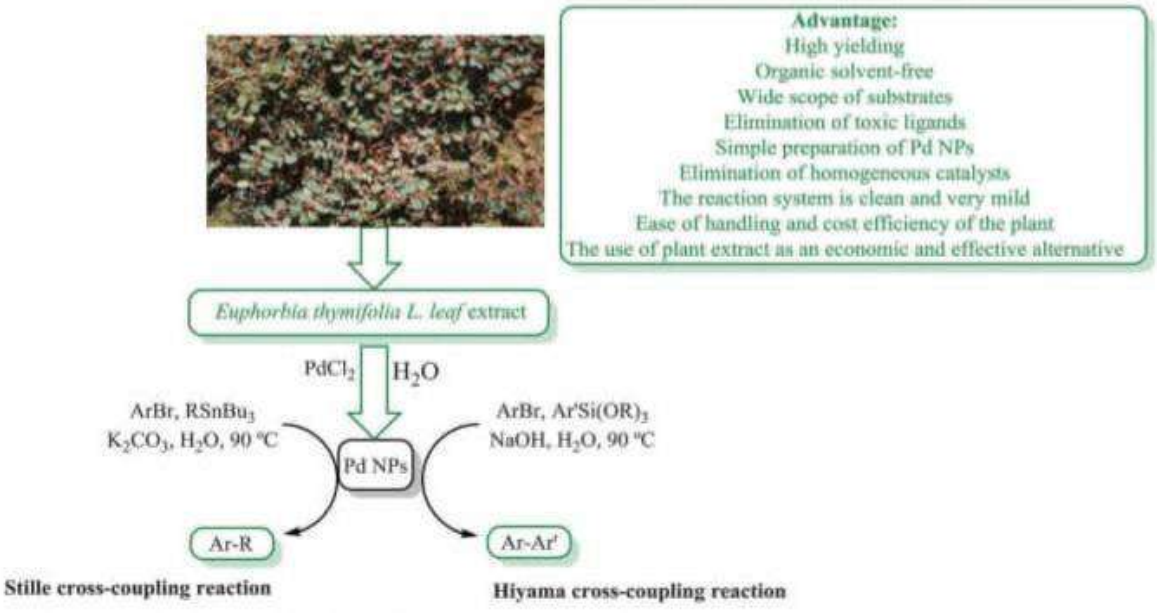


Figure-5 Mechanism of PdNPs green synthesis ; oxidation of the phenol by metal ions to alpha, beta-unsaturated carbonyl groups

Figure-6 The new strategy for ligand-free style and Hiyama cross-coupling reaction



A solution containing [Pd(NH3)4]Cl4 (Aldrich) (0.0002 M) and sodium polyacrylate(PANa, average molecular mass of 2100 Da; Fluka) (monomer unit concentration in the solution of 0.001 M) was deaerated using an NVR-4.5 D sliding vane rotary vacuum pump(vakma) equipped with a liquid nitrogen trap at residual pressure = 0.015 Torr = 2.0 Pa. Then, the solution was placed into a quartz cell and irraadiated by UV light of a low-pressure xenon flash lamp at a total flow intensity of 1UV =0.001 E/S: As a result, Pd(II) ions were completely reduced : All solution were prepared in deionized triply distilled water[24] (specific resistance of 17.0 ohom.m)

Palladium hydrosols with different particle sizes were obtained by using hydrogen to saturate a preliminary deaerated solution containing seed nanoparticles ([Pd(0)coll] = 0.0001 M) [24], a necessary amount of inicial complex of palladium ([Pd(II)] = (0.0001 to 0.0004) M), and PANPs as a stabilizer ; Pd(II) ions were reduced with hydrogen in a special unit equipped with a quartz cell for optical measurements ; the examined solution volumes were 5.0 to 20.0 mL

Catalytic activity :

In order to illuminate the catalytic activity of the synthesized PdxAg1-x nanoporous nanoalloys along with pure PdNPs, dehydrogenation of formic acid were investigateed at room temperature[6]. Fig-1 show the comparative catalytic activities of pure Pd and its nanoalloys(PdxAg1-x) towards hydrogenation from formic acid decomposition. It is clearly seen except Pd0.75Ag0.25 NPs, the other nanoalloys have much higher capacity of formic acid dehydrogenation compare to pure PdNPs. The rate of formic acid decompositions closely follow the first order kinetics and the Pd0.5Ag0.5 nanoalloy gives the highest rate of gas generation (5.84 L/hg). It is believed that the Pd0.5Ag0.5 catalyst will provide a process of preparing hydrogen gas in-situ, in other words, instantly upon demand of a selected, hydrogen consuming device or process.

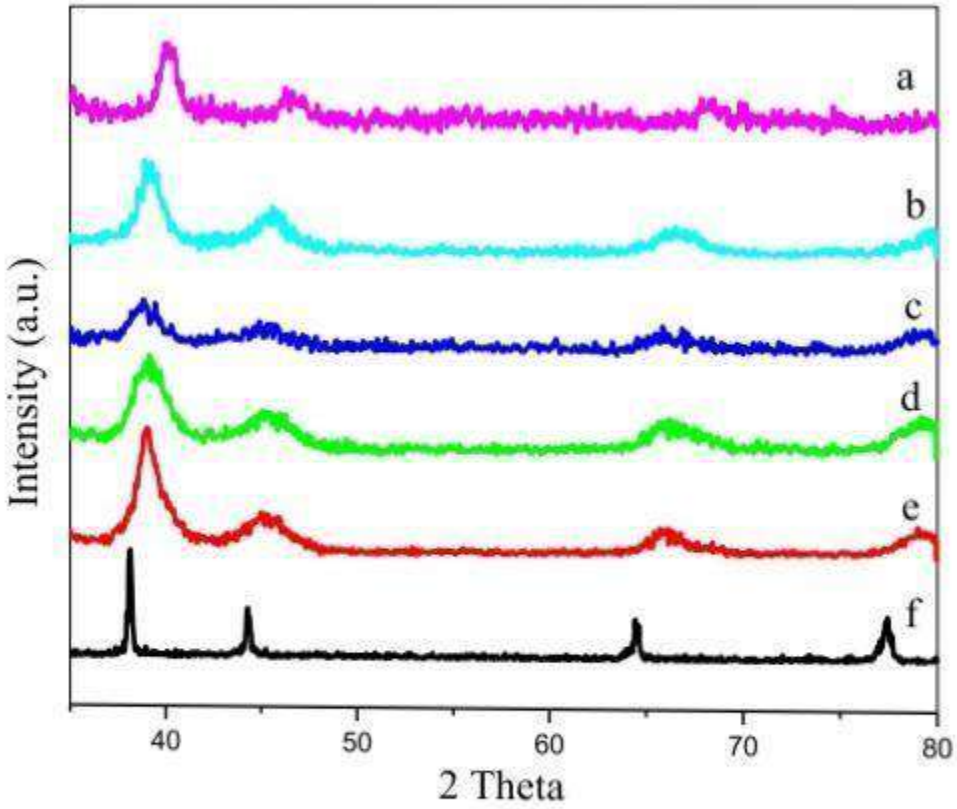


Fig. 1 – XRD patterns of the (a) Pd, (b) $Pd_{0.75}Ag_{0.25}$, (c) $Pd_{0.67}Ag_{0.33}$, (d) $Pd_{0.6}Ag_{0.4}$, (e) $Pd_{0.5}Ag_{0.5}$ and (f) Ag NPs.

Figure- 3 **Figure-4**

Figure- 3 Gas generation by decompositions of FA (0.5 M ; 10 ml) in presence of (a) Pd (b) Pd0.5Ag0.25, (c) Pd0.67Ag0.33,(uncalcined), (f) Pd0.5Ag0.5(calcined at 90 C), and (g) Pd0.5Ag0.5 (uncalcined) NPs, (ncatalys/nFA = 0.02) at 298 K

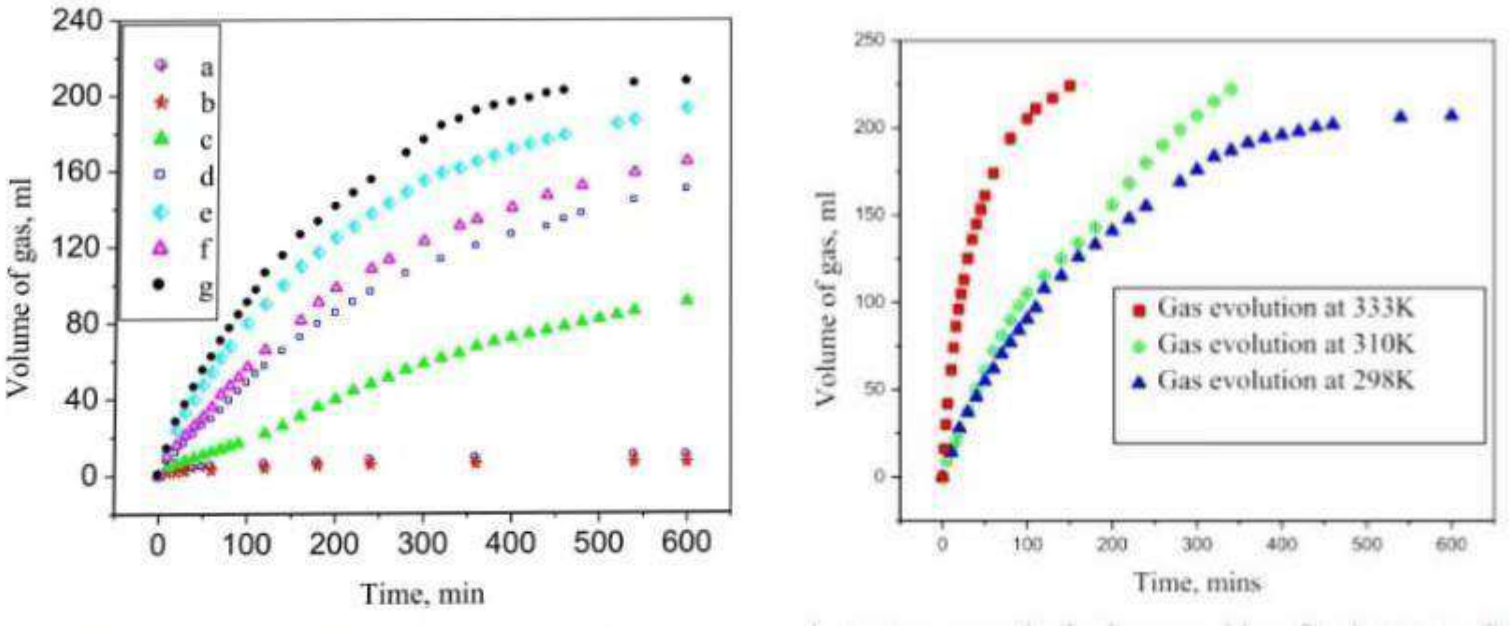


Figure- 4 Gas generation by decompositions of FA (0.5 M, 10 ml) in presence of Pd0.5Ag0.5 catalyst (ncatalyst/nFA = 0.02) at different temperature

Room temperature synthesized highly active bimetallic Ni60Pd40 nanocatalyst with large surface area(150 m^2/g) exerts 100 % selectivity towards hydrogen generation (3 equivalents of gas in 60 minutes) from hydrous hydrazine under alkaline and ambient reaction conditions. This low noble metal content catalyst offers a new prospect for on-board hydrogen production system[5].

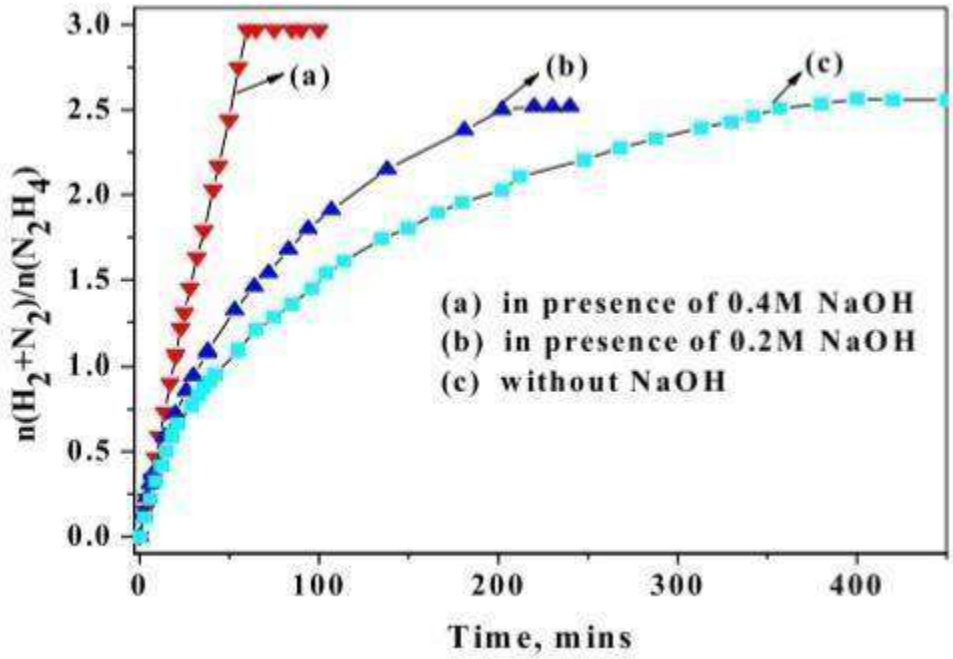


Figure-2 Time profile decompositions of 10 ml of 0.5 M hydrous hydrazine (hydrazine: catalyst = 10:1) using Ni60Pd40 BMNPs at 298 K. NaOH acts as promoter for complete hydrazine decomposition

Ultrafine palladium nanoparticles(PdNPs) with 8 and 3 nm sizes were effectively fabricated intrizine functionalized porous organic polymer(POP) TRIA that was developed by nanoaqueous polymerization of 2,4,6 triallyoxy-1,3,5-triazine[1] The PdNPs encapsulated POP(Pd-POP) was fully characterized using several techniques. Further studies revealed an excellent capability of Pd-POP for catalytic transfer hydrogenation of alkenes at room temperature with superior catalytic performance and highly pressure and temperature used in conventional hydrogenation reaction was not needed in the present synthetic system. Catalytic activity is strongly dependent on the size of the encapsulated PdNPs in the POP. The Pd-POP catalyst with PdNPs of 8 nm in diameter exhibited higher catalytic activity for alkene hydrogenation as compared with the PdPOP catalyst encapsulating 3 nm PdNPs. Computational studies were undertaken to gain insights into different catalytic activities of these two Pd-POP catalyst. High reusability and stability as well as no Pd leaching of these Pd-POP catalysts make them highly applicable for hydrogenation reactions at room temperature.

Conclusion :

This project work presents a successful synthesis of palladium nanoparticles in various way. The Ni60Pd40 nanocatalyst presented here with a high performance catalyst system with low noble metal content offer a new prospect for on board hydrogen generation. The synthesisized nanoporous Pd0.5Ag0.5 nanoalloy catalyst significantly improve the kinetics properties for a catalytic dehydrogenation of FA at room temperature as well as etelevated temperature. It is believed that the Pd0.5Ag0.5 catalyst will provide a process of preparing hydrogen gas in-situ, in other words, instantly upon demand of a selected hydrogen consuming device of process. PdPOP catalyst make them highly applicable for hydrogenation reactions at room temperature.

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Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit

Project Work

Submitted for partial fullfillment of the B.Sc. Degree in Chemistry

By

Tanmoy Das

Under the supervision of Dr. Bipul Mondal

Tanmoy Das
Reg. No.- A01-1112-112-019-2019

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I am also very much thankful to our respected teachers, whose valuable teaching and research ideas have continuously motivated me. I am also thankful to all other respected staff members of our department.

Finally, my deepest admiration goes to my parents for their all-out support throughout my life.

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Rahara, Kolkata-700118

Date: 15/01/2022

Place: Rahara

RAMAKRISHNA MISSION VIVEKANANDA CENTENARY COLLEGE

RAHARA, KOLKATA – 700118

To Whom it may concern

This is to certify that the project entitled "Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit" is the result of review work done by Mr. Tanmoy Das , who has registered his name in "Ramakrishna Mission Vivekananda Centenary College (Autonomous), Rahara, Kolkata-700118, in undergraduate level. This work has been carried out under my supervision in this college.

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Preparation, Characterization and Chemistry of dinuclear hydrazonato-Vanadium(V) complexes with $[OV(\mu\text{-}O)VO]^{4+}$ unit

ABSTRACT

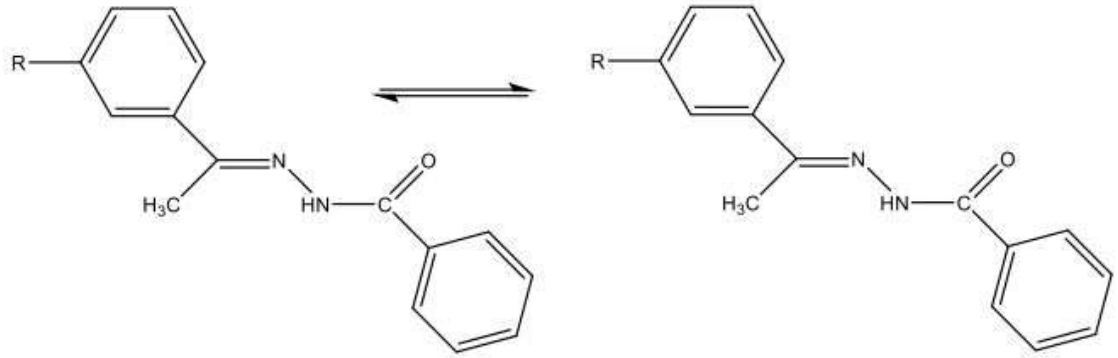
Dinuclear trioxidic $[(VOL)_2\mu\text{-}O]$ (1-4) complexes were synthesized from the reaction of $[VO(acac)_2]$ with an equimolar amount of H_2L [H_2L is the general abbreviation of hydrazone ligands (H_2L^{1-4}) in which the two H's representing the dissociable phenolic and amide protons, derived from the condensation of benzoyl hydrazine with either 2-hydroxyacetophenone or its para substituted derivatives] in acetone or dichloromethane or acetonitrile. These $V_2O_3L_2$ complexes were also obtained from the reaction of $VOSO_4$ with H_2L in the presence of two equivalents sodium acetate in aqueous-methanolic (50% V/V) medium and also from the decomposition of $[V^{IV}O(L)(bipy/phen)]$ complexes in CH_2Cl_2 solution. Black monoclinic crystals of 2 and 4 with C2/c space groups were obtained from the reaction of $[VO(acac)_2]$, respectively with H_2L^2 and H_2L^4 in acetone in which the respective ligands are bonded meridionally to vanadium in their fully deprotonated enol forms.

These dinuclear complexes are converted to the corresponding mononuclear cis *dioxido* complexes $K(H_2O)^+[VO_2(L)]^-$ (5-8) and mixed ligand [VO(L)(hq)] complexes on rection with 2 equivalent KOH in methanol and 2 equivalents 8-hydroxyquinoline in chloroform. Ascorbic acid reduces the dioxovanadium(V) complexes reversively under aerobic condition.

INTRODUCTION

Vanadium is an interesting transition element is relatively abundant (~ 0.015% of earth's crust) in nature and is present in plant and animal cells [1] at concentration 10-20 nM. Among the wide range of possible oxidation state -III to +V, Vanadium easily switches between +IV and +V and the stabilization of either of these two states under aerobic condition depends upon the basicity of the coordinated ligand and also on the pH of the reaction medium. The +V state has received considerable attention probably due to its two important properties: (i) it can exist in three motifs *viz*., mononuclear VO^{3+} and VO_2^+ motifs and dinuclear $V_2O_3^{4+}$ motif and (ii) it could exist in either 5 or 6 coordinated environment. These motifs are stable in solution around the physiological pH(~7) only when the metal is coordinated with sufficiently strong ligand for preventing the precipitation of hydroxides. The objectives of this review: (i) to synthesize the complexes containing $V_2O_3^{4+}$ core with a family of hydrazone

ligands, (ii) To study the various synthetic routes for the formation of such type of complexes, (iii) To examine the feasibility of conversion of these dinuclear complexes into the mononuclear complexes with VO^{3+} and VO_2^+ motifs and (iv) to study the electronic effect of para substituents in the hydrazone ligands on the vanadium in these complexes. Here the four tridentate dibasic hydrazone ligands H_2L^{1-4}, have been used, derived from the condensation of benzoyl hydrazine with 2-hydroxyacetophenone and its para-substituted derivatives.



R	H_2L
H	H_2L^1
CH_3	H_2L^2
OCH_3	H_2L^3
Cl	H_2L^4

Fig. 1

SUMMARY OF THE PROJECT WORK

Synthesis of H_2L^{1-4}

These hydrazone ligands derived by the condensation of benzoyl hydrazine with 2-hydroxyacetophenone and its 5-substituted derivative [2,3] in methanol. In the free state, these are present in their keto-form but they undergo complexation through their completely enol form as indicated by their IR and ^{1}H NMR spectra.

Synthesis of the complexes $[V_2O_3L_2]$ (1-4)

All dinuclear trioxide $[V_2O_3L_2]$ complexes were synthesized by different methods using various starting materials, *viz.*, (i) equimolar amount of $[V^{IV}O(acac)_2]$ and H_2L under refluxing condition in non-hydroxylic solvent [3] e.g., acetone, CH_2Cl_2, acetonitrile etc.; (ii) by reacting $VOSO_4$ with equimolar amount of H_2L in presence of two equivalents sodium acetate in aqueous-methanolic medium [3] and (iii) by the decomposition [4] of $[V^{IV}O(L)(bipy/phen)]$ complexes in non-hydroxylic solvent like CH_2Cl_2, $CHCl_3$, C_6H_6 etc. In

all the above methods the starting materials are different tetravalent precursors, and the oxidizing agent is most likely the aerial dioxygen. These reactions are represented by the following equations 1, 2, 3:

$$2[V^{IV}O(acac)_2] + 2H_2L + \tfrac{1}{2}O_2 \rightarrow [V^{V}_2O_3L_2] + 4Hacac \quad \text{- - - - - - - - - - (1)}$$

$$2VOSO_4 + 2H_2L + 4CH_3COONa + \tfrac{1}{2}O_2 \rightarrow [V^{V}_2O_3L_2] + 2Na_2SO_4 + 4CH_3COOH \text{ - - - (2)}$$

$$2[V^{IV}OL(bipy/phen)] + \tfrac{1}{2}O_2 \rightarrow [V^{V}_2O_3L_2] + 2(bipy/phen) \text{ - - - - - - - - -- (3)}$$

Where Hacac, bipy and phen are representing respectively acetylacetone, 2,2'-bipyridine and 1,10-phenanthroline.

Monoclinic crystals of $[V_2O_3(L^2)_2]$ (Fig. 2) and $[V_2O_3(L^4)_2]$ (Fig. 3) with *C2/c* space group were obtained by following the above-mentioned preparative method (1), while orthorhombic crystals of $[V_2O_3(L^2)_2]$ (Fig. 4) with *Pbca* space group were obtained by adopting the preparative method (3). The analytical, spectral (IR, UV-vis and 1H NMR) and electrochemical data of these two dimorphs are identical (within experimental error). The solid-state structural features of these dimorphs differ in crystal packing and in the molecular symmetry. In the monoclinic variety, two structurally very similar but crystallographically distinct respective molecules are present in both the crystal lattices of $[V_2O_3(L^2)_2]$ and $[V_2O_3(L^4)_2]$ with the bridging oxygen lying on a crystallographic 2-fold axis such that the two halves of each of the two molecules are crystallographically equivalent while in the orthorhombic variety of $[V_2O_3(L^2)_2]$, discrete molecules constitute the crystal lattice and the bridging atom has no crystallographic symmetry but two halves of the molecule have closely matching dimensions. However, in both varieties the geometry at metal center is a distorted square-pyramid with the meridionally disposed respective hydrazone ligand in enol form. The bridging oxo-oxygen occupies the fourth position of the square plane and the terminal oxo-oxygen is occupied in one of the two axial positions. The two terminal oxygen atoms O(1) and O(1)$1 (for the crystals with *C2/c* space group) or O(1) and O(1a) (for the crystals with *Pbca* space group) are mutually *trans* lying on opposite sides of the V−O−V plane. The extent of distortion is different for each of the vanadium centers even within the same structure. The V-O bond lengths follow a general order: $V-O^t$ (t = terminal) < $V-O^b$ (b = bridging) < $V-O^p$ (p = phenolic) < $V-O^e$ (e = enolic). The V−O−V angles are very similar and are close to 113°, which is consistent with the reported values of analogous hydrazone complexes [5, 6, 7].

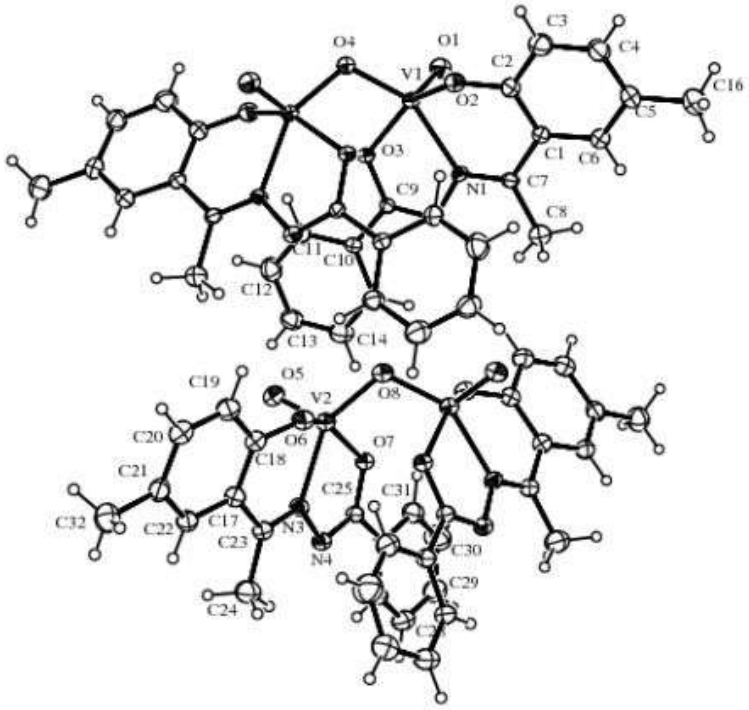


Fig. 2: Molecular structure of $[V_2O_3(L^2)_2]$ (with *C2/c* space group) with thermal ellipsoids drawn at 50% probability.

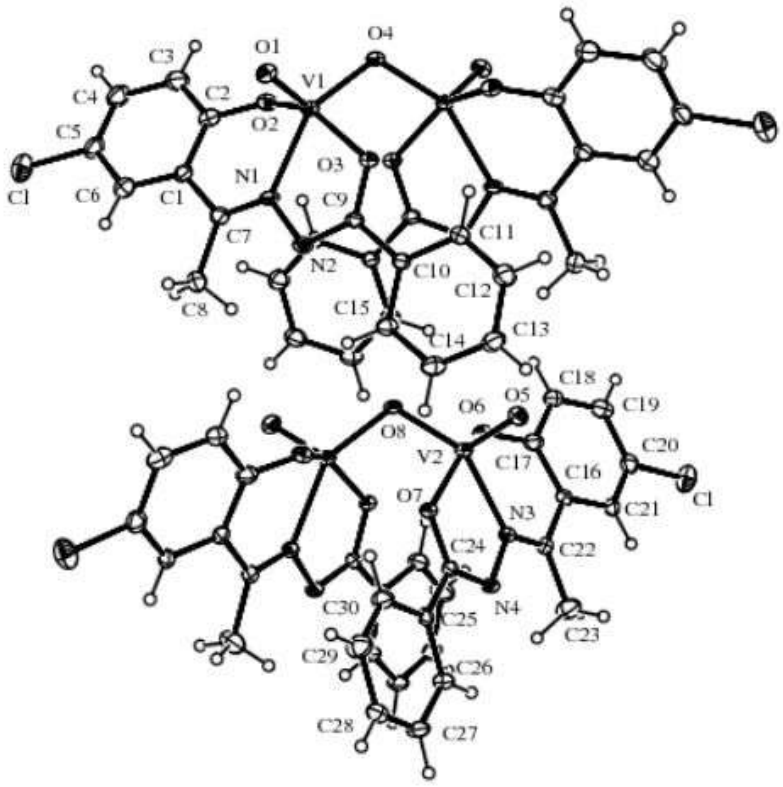


Fig. 3: Molecular structure of $[V_2O_3(L^4)_2]$ (with *C2/c* space group) with thermal ellipsoids drawn at 50% probability.

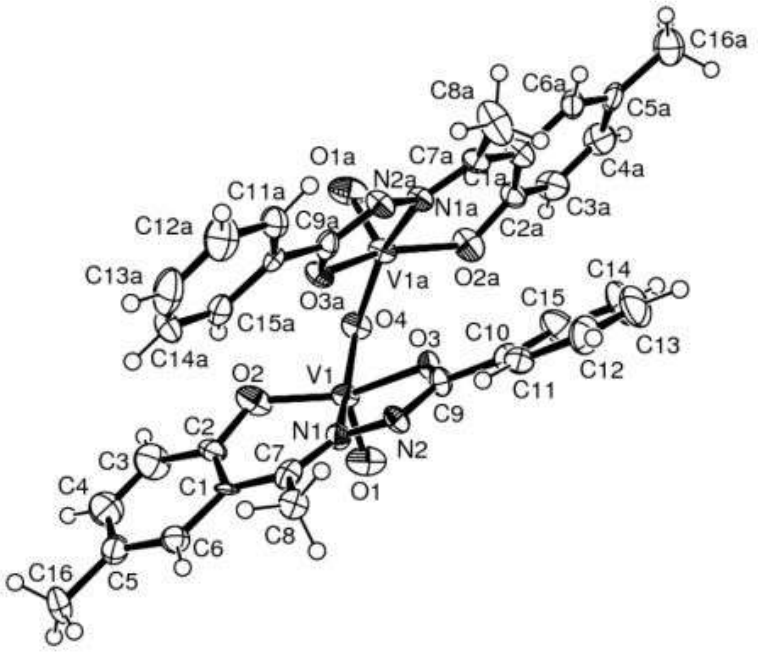


Fig. 4: Molecular structure of $[V_2O_3(L^2)_2]$ (with *Pbca* space group) with thermal ellipsoids drawn at 50% probability.

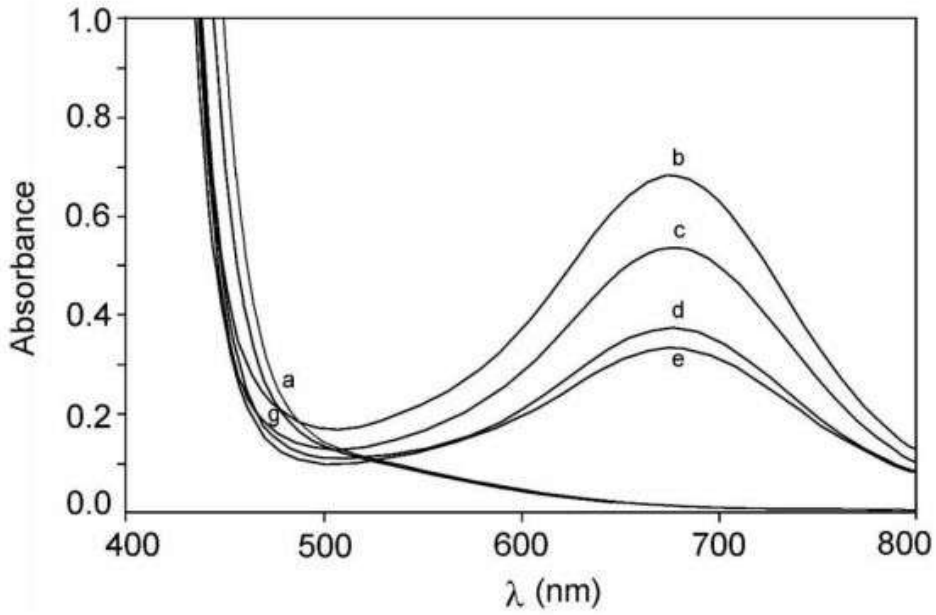


Fig. 5: Electronic spectra (400-800 nm) of a 7.973×10^{-4} mol dm^{-3} methanol solution of complex $K(H_2O)^+[VO_2L]^-$: (a) before the addition of ascorbic acid, (b) immediately after the addition of ascorbic acid, (c) 15 min after the addition of ascorbic acid, (d) 40 min after the addition of ascorbic acid, (e) 80 min after the addition of ascorbic acid and (f) 720 min after the addition of ascorbic acid. The concentration of ascorbic acid was about 10 times than that of the concentration of the complex.

Conversion of $[V_2O_3L_2]$ complexes to $K(H_2O)^+[V^VO_2L]^-$ and $[V^VOL(hq)]$ complexes

These dinuclear oxidovanadium(V) complexes can easily be converted to either mononuclear dioxidovanadium(V) complexes $K(H_2O)^+[V^VO_2L]^-$ or mixed-ligand complexes of the type $[V^VOL(hq)]$ on reaction, respectively, with two equivalents KOH in methanol and two equivalents 8-hydroxyquinoline (Hhq) in $CHCl_3$. The respective reactions are:

$$[V^V{}_2O_3L_2] + 2KOH + H_2O \rightarrow 2K(H_2O)^+[V^VO_2L]^-$$

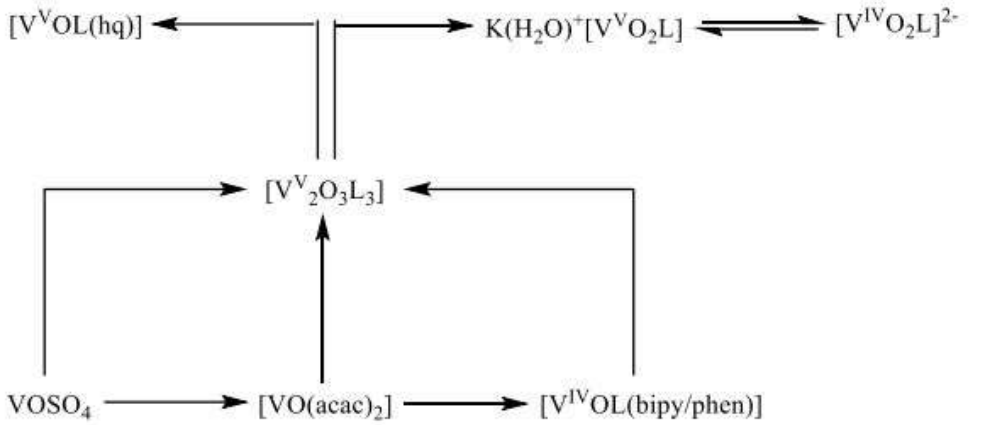
$$[V^V{}_2O_3L_2] + 2Hhq \rightarrow 2[V^VOL(hq)] + H_2O$$

Catalytic oxidation reaction of $K(H_2O)^+[V^VO_2L]^-$ complexes with ascorbic acid

The mononuclear dioxidovanadium(V) complexes oxidise ascorbic acid reversibly which was monitored spectrophotometrically. In each case after the addition of reducing agent a new band in the visible region near 675 nm was detected to a d-d transition of the resulting V(iv) species. After keeping the solution for sometime the intensity of the new band decreases gradually and finally the initial spectrum was obtained in a time interval ~ 12 hour. These observations strongly suggest that during the oxidation of ascorbic acid the dioxidovanadium(V) complexes are reduced by it to form the corresponding V(IV) complex presumably of the type $[VO_2(L)]^{2-}$ are not stable under this environment.

CONCLUSION

The four dinuclear trioxide Hydrazone complexes have been synthesized from various synthetic routes starting from different VO^{2+} precursors and these hydrazone ligands are very suitable for the stabilization of these motifs. The formation of these complexes from the decomposition of mixed ligand [VO(L)(bipy/phen)] complexes in CH_2Cl_2 solution indicates that these ligands have strong tendency for the stabilization of vanadium in its highest oxidation state(+V). These dinuclear complexes can be converted to the mononuclear binary complexes with VO_2^+ motif simply by increasing the (PH ~ 11) of the solution and mixed ligand ternary complexes with VO^{3+} motif by adding a monobasic bidentate strong chelating ligands. The dioxidovanadium(V) complexes can catalyze the reversible oxidation of ascorbic acid under aerobic condition which is biologically important particularly in relation to insulin enhancing activity.



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Alcohols as an Alternative Fuel:

A way to Achieve Sustainability

Project Work

For Partial Fulfillment of the B.Sc . Degree in Chemistry

By

Tathagata Chakraborty

Under the supervision of *Dr. Subhabrata Banerjee*

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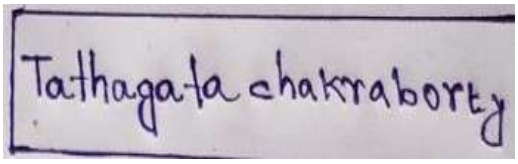
Finally, my deepest admiration goes to my parents for their all-out support throughout my life.



(Full Signature of the Candidate)

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Date : ***January 15, 2022***

Place : **Rahara**

ABSTRACT

Conventional fuels are hydrocarbon based. So, those are considered as fast depleting and harmful to the environment. In the last few decades, the synthesis of higher alcohols has drawn considerable amount of interest. Adding alcohol to the petroleum product allows the fuels to combust more completely due to the presence of oxygen which increases the combustion efficiency and consequently reduces air pollution. Alcohol as an alternative fuel works properly when one can redesign the engine or the vehicle can be redesigned or one can blend in one or more additives to the ethanol or methanol to improve its characteristics.

Catalytic conversion of synthesis gas to alcohols is advantageous, as this uses various renewable and non-renewable carbon resources. Different catalytic systems/substances can be used for synthesizing higher alcohols from synthesis gas. Depending on the process conditions and the catalyst used, the reaction mechanism varies and the products include primary and secondary alcohols of both normal and branched carbon chains. The present article presents a brief overview of the processes and use of Fe, Ni, or Co-modified catalyst for low temperature, low pressure synthesis of methanol and higher alcohols.

1. Introduction

The engine utilizing hydrocarbon fuels will continue to be the most important transportation system for next few decades. Approximately 30% of the world's greenhouse emissions currently originates from the transportation sector [*Awad et al., 2018; Dalkmann and Brannigan, 2007; Wright, 2004*]. Demand for fuel that continues to increase from customers in recent years has resulted in the depletion of fossil fuels [*Abas et al., 2015; David, 2018; Jia et al., 2018*]. Investigations about alternative fuels have been explained in the literature, where reservoirs can meet the demand for fuels such as oil, coal and natural gas [*Kessel, 2000; Zucchetto, 2004*]. The growth of the automotive industry which continues to increase, has had an impact on energy scarcity. The increasing demand for alternative fuels and the optimum use of petroleum are the biggest challenges because people want to be ensured of energy security globally.

Originally, lead was added to gasoline as an octane enhancer. For each gram of lead added to a gallon of gasoline, the octane rating goes up about 10 times or more in octane numbers. Engines require certain minimum levels of octane to run smoothly and resist knocking. Concern about leaded gasoline emissions encouraged the Environmental Protection Agency, USA (EPA) to call for reduced lead in gasoline. As unleaded gasoline became the standard, petroleum refineries looked to other additives to help keep gasoline octane numbers at leaded standards. The EPA (USA) has approved using several alcohols and ethers in unleaded gasoline. Ethanol and methyl tertiary butyl ethers (MTBE) are the two most popular additives. MTBE is not as widely used as ethanol, but refineries use it as an additive because it is not as sensitive to water as other additives and tends not to increase fuel volatility. Low molecular weight alcohols such as ethanol have replaced other additives as octane boosters in automotive fuels.

Alcohols can be promoted as alternative fuels or alternative fuel components in transportation for following reasons:

1. Both lower molecular weight alcohols can be made out of indigenous energy resources such as biomass, coal and natural gas, which are available with low cost.
2. Greenhouse gases emissions can be reduced.
3. Compared with gasoline, alcohols having higher average octane rating can increase power and fuel efficiency.
4. Decreases the releasing of toxic gases into the environment.
5. Alcohol fuels have a lower evaporative emission.
6. The overall energy efficiency of fuel can be improved.

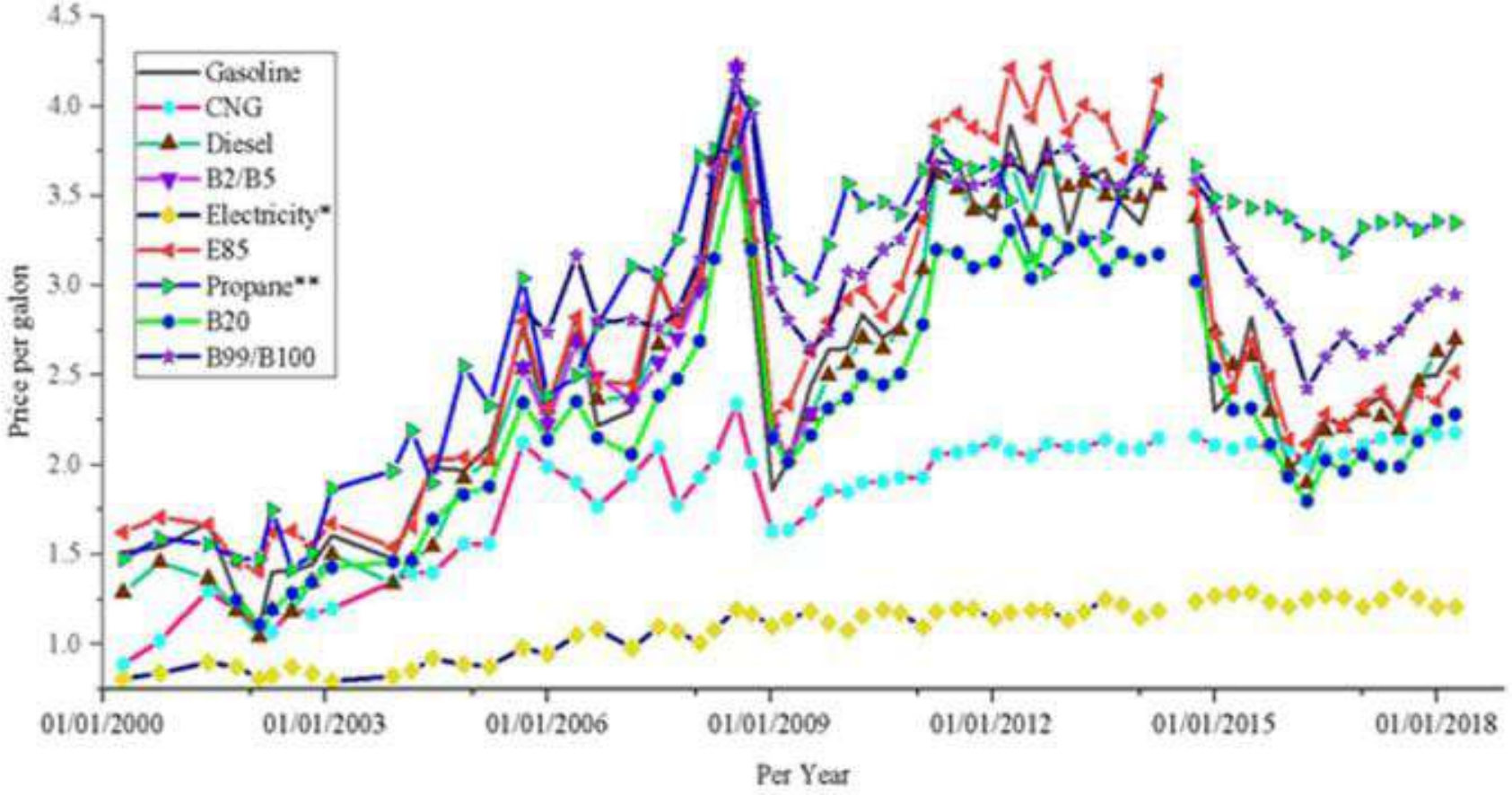


Fig. 1. Alternative fuel vehicles in use, 2000 to 2018 (Energy, 2018).

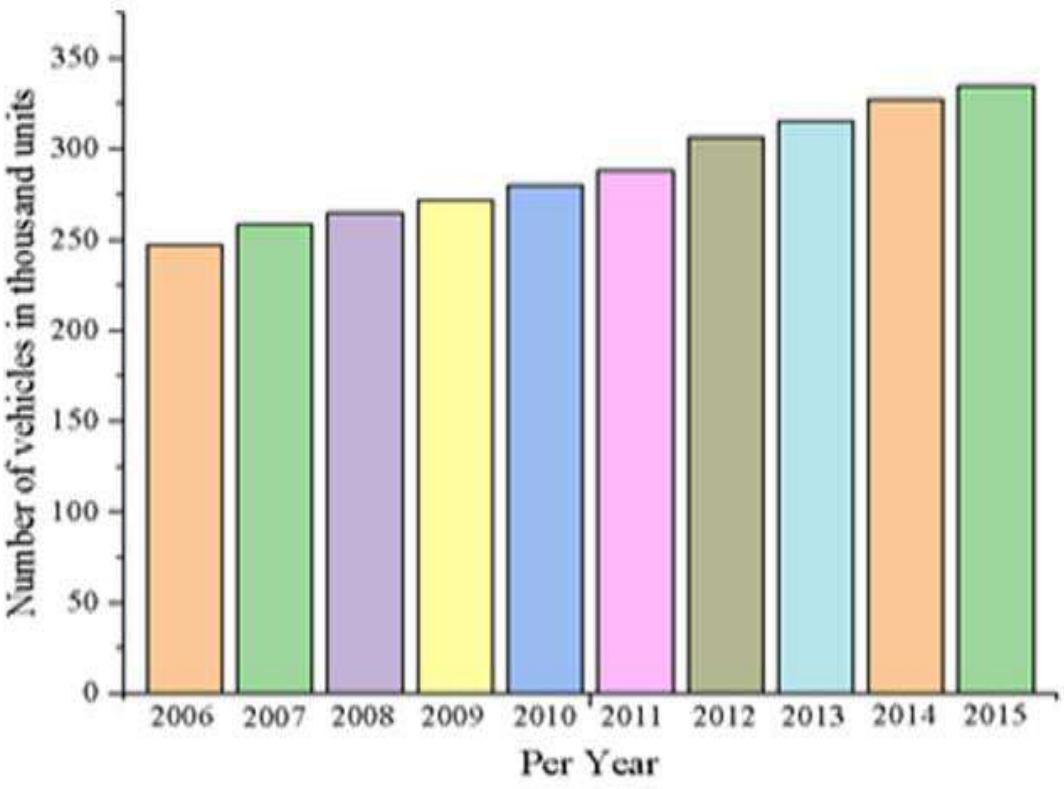


Fig. 2. Number of vehicles in thousand units (Energy, 2018).

Unlike gasoline and diesel, alcohols contain oxygen. Adding alcohols to petroleum products allows the fuel to combust more completely due to the presence of oxygen, which increases the combustion efficiency and reduces air pollution. Using gasoline blended with approximately 10% ethanol can significantly reduce greenhouse gas emissions. An additional factor making ethanol attractive as a fuel extender or substitute is that it is a renewable resource.

Table 2 compares the properties of alcohols such as boiling point, latent heat, vapour pressure and solubility in water, with those of octane and hexadecane. Compared to conventional fuels, alcohols have less combustion energy. However, the lowest stoichiometric air to fuel ratio helps alcohol fuels to produce more power inside an engine when these fuels are burned. ***Table 3*** shows the effective blending values of oxygenated fuels as gasoline blends. *Research Octane Number* (RON) is determined in test engines at a relatively low speed (600 rpm) to simulate city driving speed with frequent acceleration. *Motor Octane Number* (MON) is measured at a higher speed (900 rpm), which simulates highway driving. For most fuel components, RON is greater than MON and the difference between them is used to judge fuel quality. This is known as the sensitivity of the fuel and a maximum value is specified for the gasoline, which typically should be less than 10. Although methanol has the highest percentage of oxygen, its sensitivity is 30 when compared with

ethanol, having a sensitivity of 15 and a *Reid Vapour Pressure* (RVP) much less than that of methanol. In essence, ethanol is more advantageous when various factors such as the percent oxygen content, sensitivity, and Reid vapour pressure etc. are compared with those of other fuels.

Table 2: Characteristics of chemically pure fuels

Fuel	Chemical weight (lb/mol)	Specific gravity	Boiling point (°C)	Latent heat (Btu/lb)	Combustion energy (Btu/lb)	Vapour pressure @100 F (psig)	Solubility part in 100 parts H_2O	Stoichiometric air-fuel ratio
Methanol	32	0.79	65	503	10,260	4.6	Infinite	6.5
Ethanol	46.1	0.79	78	396	13,160	2.2	Infinite	9
Butanol	74.1	0.81	117	186	15,770	0.3	9	11.2
Octane	114	0.70	210	155	20,750	1.72	Insoluble	15.2
Hexadecane	240	0.79	287	-	20,320	3.46	Insoluble	15

Table 3: Effective blending values of the fuels

Fuel	Density (kg/l)	% of O_2 (wt%)	RON	MON	RVP (kPa)
Methanol	0.796	49.9	130	100	250
Ethanol	0.794	34.7	115	100	130
IPA	0.789	26.6	117	100	70
TBA	0.791	21.6	100	90	65
MTBE	0.744	18.2	110	100	55
ETBE	0.770	15.7	112	100	28

2. Adverse Effects of Alcohol Fuels

There is no miraculous, super fuel that will satisfy all the requirements of cost effectiveness, maximum thermal efficiency, and engine performance, and still remain clean enough to protect the environment. Every fuel has advantages and disadvantages, and selection of a particular fuel is a function of different parameters including the physical properties of the fuel. The disadvantages of the alcohol fuels might be summarized as follows:

1. *The economics of production*. Unless the cost of alcohol production from renewable resources is made cost-effective, there will be no demand for it. These alcohols could be produced from biomass, coal, and natural gas.

2. *Flame visibility of alcohol is difficult to be detected*, which might be hazardous. The lack of visibility is due to the small number of carbon atoms present in the alcohol. Since there is very little carbon, there is no soot formation to give the flame color.

3. *Cold storability problems*. Due to their low vapor pressure, high latent heat of vaporization, and single boiling point, alcohols, especially ethanol, have difficulty meeting industry standards for starting in cold weather.

4. *Phase separation occurs when alcohol and water are mixed together* in an ethanol blended fuel. When the alcohol and water get separated from the gasoline, the resulting mixture settles at the bottom of the tank and becomes corrosive.

5. Ethanol with neutral pH has little corrosive effect. If the alcohol/gasoline blend stays for a sufficiently large time inside the tank, it allows the alcohol to absorb moisture from the atmosphere and *causes corrosion* to the fuel injection system

3. Modifications Required for Best Use of Alcohol Fuels

In order to best use the alcohols as alternative fuels there are two options: redesign the engine to take full advantage of the alcohol fuel's properties or blend in one or more additives to the ethanol or methanol to improve its characteristics.

3.1 Modifications to vehicles

The following modifications are typical for converting conventional vehicles to high-level alcohol blends

I. Stainless steel fuel tank with stainless flame arrestors in the fill and vent tubes to prevent ignition by an external source.

II. Methanol resistant float level potentiometer with a corrosion protection circuit.

III. Higher flow methanol–tolerant fuel injector and fuel pump to handle higher flow rates.

IV. Stainless fuel lines with accompanying Teflon fuel hoses.

V. Anodized aluminium fuel injection rail and modified pressure regulator.

3.2 Additives required for improving the fuel properties of alcohols

Alcohols can be used effectively as alternative liquid transportation fuels by modifying their properties by using certain additives, which must be physically and chemically compatible with the base alcohol fuel and have the same or higher specific energy content. Additives must not be readily removable from the fuel, significantly add to exhaust emissions, or leave any residue. They should not complicate regulatory compliance, and they should be relatively inexpensive. Ethanol

and methanol are completely miscible with water, but show very poor miscibility with gasoline containing traces of water. So, blending gasoline with ethanol or methanol in the presence of water may lead to a phase separation problem. Additives such as higher alcohols like iso-propanol, 1-butanol, n-decanol, various commercial non-ionic surfactants, and various anionic fatty acid surfactants can be effectively controlled to prevent the phase separation problem. The prevention of phase separation would have definite benefits for overall drivability, as well as in corrosion of water-sensitive components such as aluminium. Conventional fuel injection systems usually encounter lubrication problems due to the low viscosity of alcohol fuels, which leads to wearing of the engine parts. Higher alcohol additives offer better lubrication and decrease wear in engine parts. During combustion, alcohol blended fuels produce acids that are responsible for wearing of engine parts. Neutralizers such as zinc dialkyldithiophospates and calcium sulfonates are added in lubricant oil to neutralize these acids and improve lubrication. Shorter lubricant oil change intervals reduce corrosive wear significantly.

4. Production of methanol

The simplest form of alcohol is methanol, it is also known as methyl alcohol, wood alcohol, or wood spirits, is frequently abbreviated as MeOH. It is a colorless, volatile, flammable liquid with a distinctive odor and polar liquid at room temperature. Methanol was miscible with gasoline or petrol, water and most of the organic compounds. It can be synthesized by different methods.

4.1.1 Synthesized from biomass

MeOH can be synthesized industrially from biomass like plants, fruits and animal wastes through anaerobic metabolism by many bacteria. Also, methanol was formed as a by-product during the ethanol fermentation process. Moreover, mainly in China and South Africa methanol can be produced from coal because of majority coal deposits was found in both countries and throughout the world. Most of the industrialists preferred for synthesis of MeOH from biomass due to process simplification, reduction of cost and energy consumption. The production scheme of methanol has been shown below.

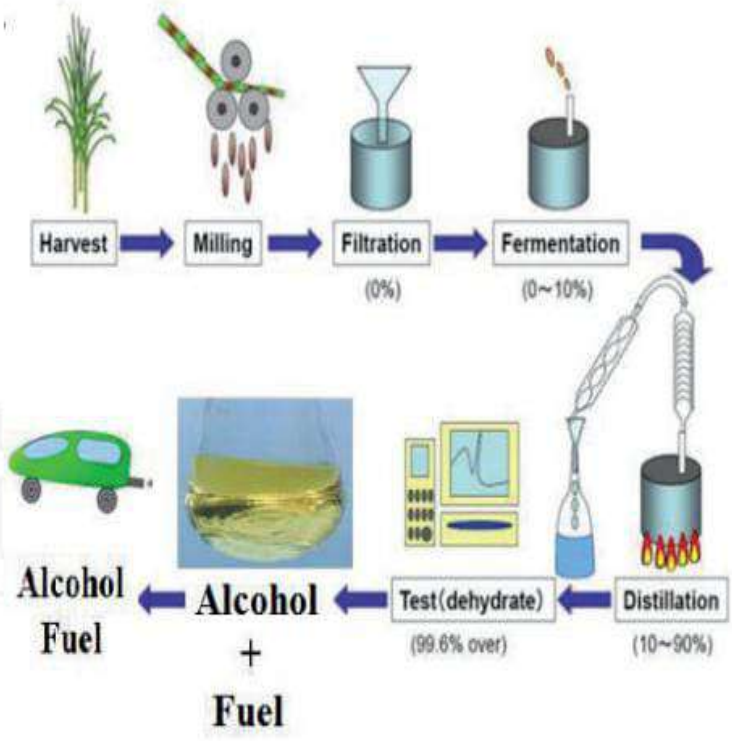
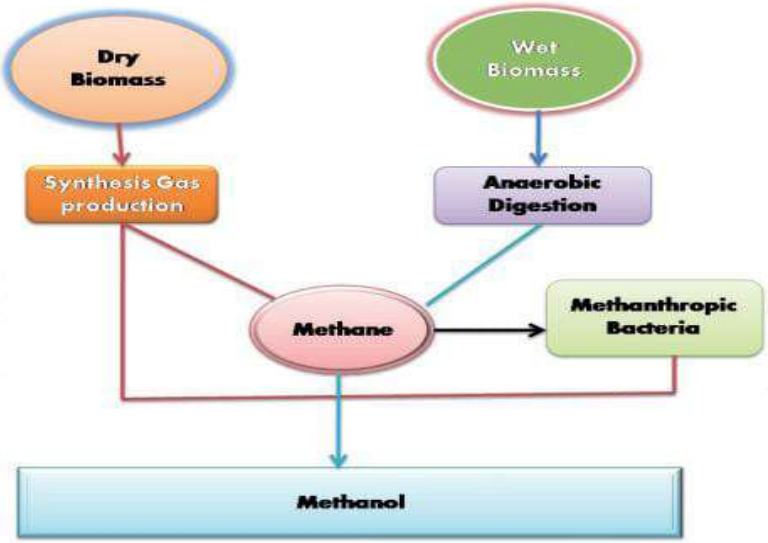


Figure 3.

4.1.2 Methanol from catalytic synthesis

The reactions relevant for the production of methanol have been known for a longtime. A mixture of CO_2, CO and H_2 can react with each other to form methanol and water as a byproduct. Equations (1) and (2) show the stoichiometry of these reactions and their reaction enthalpy.

$CO + 2H_2 \leftrightarrows CH_3OH$ ΔH (at 298.15 K & 5 MPa) = − 90.7 $kJmol^{-1}$



5. Synthesis of higher alcohols from synthesis gas

The synthesis of higher alcohols from synthesis gas by direct catalysis was recognized in 1923 by *Frans Fischer* and *Hans Tropsch*. They reported that a mixture of alcohols, aldehydes, ketones, fatty acids, and esters were formed when the reaction between CO and H_2 was performed at pressures ranging from 10 to 14 MPa and at temperatures of 400–500 ◦C in the presence of an alkalized iron oxide catalyst. They named the mixture synthol and named the process the synthol process .

In 1930, Frolich and Cryder reported the formation of alcohols higher than methanol by passing syngas over a Zn : Mn : Cr (= 1.0 : 1.1 : 1.03) catalyst. They reported that methanol forms from a formaldehyde intermediate and that the higher alcohols form from the methanol through a stepwise condensation reaction.

In the 1940s, Du Pont developed an alkalized Mn-Cr catalyst to synthesize methanol and higher alcohols from syngas for commercial purposes. In the late 1940s, Farbenindustrie et al. introduced the Synol process for the manufacture of alcohols from syngas. This process uses low pressures of around 2 MPa with higher productivity of alcohols by modifying the Fischer–Tropsch alkalized iron catalyst. Natta et al. reviewed the synthesis of higher alcohols from CO and H_2, in 1957 and reported that the synthesis of higher alcohols was always related to the presence of strongly basic substances.

6. Catalyst systems for higher alcohols synthesis

Several authors summarized typical operating conditions, research status, characteristics, and performance of primary groups of catalysts that have been adapted and tested for higher alcohol synthesis (HAS). According to these reviews, there are two major catalyst groups for higher alcohol production:

6.1 Modified methanol synthesis catalysts

a. Alkali-modified high pressure, high temperature methanol synthesis catalysts.

b. Alkali-modified low pressure, low temperature methanol synthesis catalysts.

6.2 Modified Fischer–Tropsch catalysts

a. Fe, Ni, or Co-modified low temperature, low pressure methanol synthesis catalysts.

b. Supported rhodium-group catalysts. c. Alkali-modified molybdenum-based catalysts.

6.3 Fe, Ni, or Co-modified low temperature, low pressure methanol synthesis catalysts

In 1934, Taylor modified the hydrogenation action of Fischer–Tropsch (F–T) catalysts by the addition of metal sulfides, borates, phosphates, and/or alkali promoters. In

1952, Anderson et al. proved that alkali-promoted F-T catalysts improved the production of higher alcohol synthesis. Later studies showed that decreased operating temperatures and increased reactant stream contact time reduced the hydrocarbon production and favoured the alcohol formation over Fe- and Co-containing F-T catalysts. Typical operating conditions for these catalysts are 4–10 MPa of pressure, 200–350◦C of temperature, and 2000 – 8000 L(STP)/[(kg of catalyst) h] of gas hourly space velocity (GHSV) with a ratio of H_2/CO of 1.0 to 2.0. The products consist mainly of linear alcohols, with small amounts of branched alcohols. Linear alcohol distribution obeys the Schulz–Flory distribution, but the formation of hydrocarbons cannot be reduced to acceptable levels over these catalyst systems. Deactivation causes the destruction of the spine structures of Cu and Co, Ni or Fe and these cannot be used at temperatures greater than 300 ◦C due to the sintering of Cu [**34**]. High temperature and pressure could increase carbon deposition from the iron group metals, resulting in catalyst disintegration. The carbon deposition rate of cobalt and nickel catalysts is prohibitively high at temperatures above 250 and 300 ◦C for iron. Hydrogen-rich synthesis gas should be used in order to minimize carbon deposition [**39**]. F-T catalysts prepared from solutions of various cyanide complexes showed a slightly higher alcohol production than the conventionally prepared bimetallic catalysts [40]. The selectivity of higher alcohols was increased greatly when nickel and cobalt were added, compared with that of the CuMn/ZrO_2 catalyst. The addition of Fe to the CuMn/ZrO_2 catalyst improved its selectivity to hydrocarbon. The effect of iron was greatly influenced by the method of catalyst preparation. The presence of iron affects the structural properties of the catalyst by increasing the dispersion of copper and by improving the stabilization of the catalyst. The co-precipitation method produced highly dispersed copper species, which favoured the synthesis of methanol and branch alcohols. The wetness impregnation method gave rise to a highly dispersed copper and copper-iron phase, which showed a good performance for synthesis of straight chain alcohols . Typical activities of Fe, Ni, or Co-modified low temperature, low pressure methanol synthesis catalysts towards alcohols are reported in the literature and are shown in **Table 3**. It can be observed from this table that the calcination temperature strongly influenced the interaction between the active species (Cu and Mn) and support (ZrO_2), hence influencing the structure and catalytic performance. Xu et al. and Chu et al. observed that addition of Fe, Co to low pressure, low temperature methanol synthesis catalysts decreased CO conversion, and total alcohols yield, whereas, the selectivities of hydrocarbons and total alcohols are greatly improved. Conversely, Zhao et al. reported that addition of Ni to CuMn/ZrO_2 improved the CO conversion and hydrocarbons yield, and decreased the total alcohols yield and selectivity.

Table 3: Comparison of the activities of Fischer–Tropsch elements (Fe, Ni, or Co)-modified low temperature, low pressure methanol synthesis catalysts

	Reference						
	Xu et al. [43]	Xu et al. [43]	Xu et al. [43]	Zhao et al. [41]	Chu et al. [44]	Chu et al. [44]	Chu et al. [44]
Catalyst	$CuMnZrO_2$ (calcination temperature = 350 °C)	$CuMnZrO_2$ (calcination temperature = 800 °C)	Fe-$CuMnZrO_2$ (calcination temperature = 350 °C)	Ni-$CuMnZrO_2$	$CuLa_2Zr_2O_7$	5% Co on $CuLa_2Zr_2O_7$	3% Mo and 5% Co on $CuLa_2Zr_2O_7$
Temperature (°C)	300	300	300	300	270	270	270
Pressure (MPa)	8.0	8.0	8.0	6.0	6.0	6.0	6.0
H_2/CO molar ratio	2.0	2.0	2.0	2.0	2.0	2.0	2.0
GHSV (h^{-1})	8000	8000	8000	5000	4000	4000	4000
CO conversion (%)	37	8	29	51	38	13	20
STY of total alcohols (g/ml_{cat} h)	0.850	0.120	0.420	0.180	-	-	-
STY of higher alcohols ($g/m\ l_{cat}$ h)	0.053	0.009	0.076	0.350	-	-	-
Total alcohols selectivity (% of C)	64	44	29	55	~14	36	53
Hydrocarbon selectivity (% of C)	18	30	44	24	5.5	64	47

7. Conclusions

The production of alcohol fuel has gradually increased and become an important industry in various countries such as the United States, Brazil, and China. Methanol was produced from biomass or coal and natural gas while ethanol is mainly produced from food crops or sugarcane molasses by fermentation process. So that, rural area's sugarcane industry is one of the major industrial corridors, meanwhile the agriculture economy was increased and generates employment for more people by the collaborating with sugar industry either directly or indirectly. . Catalytic conversion of synthesis gas to alcohols is advantageous as this uses various renewable and non-renewable carbon resources. Different catalytic systems can be used for synthesizing higher alcohols from synthesis gas.

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A LITERATURE SURVEY ON SUPPORTED PALLADIUM CATALYSTS IN HECK REACTIONS

Project Work

Submitted for Partial Fulfillment of the B.Sc Degree in Chemistry

By

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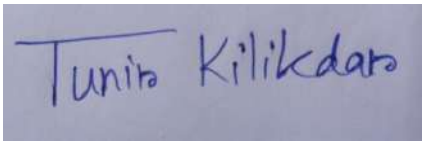

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Date: 18.12.2021

Place: Kolkata

CERTIFICATE

Date: 27.01.2022

This is to certify that the project work entitled "A Literature Survey on supported palladium catalysts in Heck reactions" submitted by **Mr.Tunir Kilikdar** (Registration No. A01-1112-112-003-2019) for the partial fulfilment of the B. Sc degree in Chemistry at Ramakrishna Mission Vivekananda Centenary College, Rahara has been executed under my supervision.

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➢ ABSTRACT:

C-C coupling reactions are important group of reactions in academic as well as in industrial fields like fine chemicals or pharmaceutical industries. Palladium has been employed as catalyst in these types of reactions in various methodologies. Nowadays, a huge number of new palladium complexes and organometallic compounds arebeing used for carbon-carbon coupling reactions in particular of Heck type reactions. It is the aim of this short literature review to report on the progress in this field of Heck type carbon-carbon coupling reactions. We will also try to summarize the approach, problems, potential and recent advances related to heterogeneously catalyzed Heck Coupling Reaction.

➢ INTRODUCTION:

There are quite some differences between homogeneous and heterogeneous catalysts. The first one includes the catalyst and the reactants in the same phase where the latter will have reactants and catalyst in different phases. Homogeneous catalysts have a higher conversion rate due to better selectivity but the separation is very difficult at the same time. For the latter one the catalyst is easily separable but sometimes may show lower activity. Both catalysts have their advantages and shortcomings.

Heck reaction, after originally discovered by Heck and Mizoroki, became an important tool for fine chemical synthesis and industrial applications [1-4]. Originally, the coupling of an aryl halide and an olefin was performed using a homogeneous Pd(0) complex in the presence of base but later the scope of the Heck reaction has been extended. Heck reaction soon became an important tool for fine chemical synthesis and industrial applications. Originally, the coupling of an aryl halide and an olefin was performed using a homogeneous Pd(0) complex in the presence of a base. Several solvents are widely applied in Heck reactions. The most promising combination of solvent and base depends strongly on the catalytic system. Solubility of the base and its basicity in the respective solvent must also be taken into account.

In this brief review work,we shalldiscuss about application of some major supported heterogeneous palladium catalysts for Heck coupling reactions and about the potential applications of Heck catalysis for organic synthesis and fine chemical productions.

➢ SUMMARY OF THE WORK:

After the discovery of the reaction by Heck and Mizoroki, Pd black was identified as an active catalyst for the conversion of iodobenzene [5,6]. Mizoroki concluded already that Pd black was only a kind of precursor for the active Pd species. Starting from the mid 1990's, observations on different aspects of heterogeneous or homogeneous character of the reaction are reported. The main three approaches are: (i) The flat Pd surface activates a reacting molecule for the attack of the reaction partner. (ii) Occuring at defective sites on the metal surface. (iii) The actual active species is Pd in solution, molecularly dissolved by leaching from the solid material.

So, the mechanism would be homogeneous, where the solid catalyst serves only as a reservoir for active Pd species in solution which is already proposed by Mizoroki [5]. The second mechanism was supported first by Augustine and O'Leary. The probably first experimental results were reported by Shmidt and Mametova [7]. They showed that for the reaction of iodobenzene and methyl acrylate relies on the Pd amount in solution and that Pd is re-precipitated onto the support at high conversion of iodobenzene. The nature of the various Pd species, their conc., other important factors, duration of the reaction in heterogeneously catalyzed Heck reactions have been showed in the following two tables

Table 1: Selected heterogeneously catalyzed Heck reactions of iodobenzene [29].

Entry	Catalyst	Cat. Conc. [mol%]	Alkene	Solvent	Base	T [°C]	t [h]	Yield [%]
1	Pd nanoclusters	0.2	BA[a]	DMA	NaOAc	120	24	75
2	Pd/polymer	0.0008	styrene	DMA	NBu_3	140	90	99
3	Pd/polymer	0.005	BA	toluene	NEt_3	100	20	98
4	Pd/polymer	0.01	styrene	CH3CN	NBu_3	90	2	98
5	Pd/polymer	0.1	styrene	DMF	KOAc	90	6	93
6	Pd/polymer	0.1	MA[b]	dioxane	NEt_3	100	2	99
7	Pd/polymer	0.67	styrene	water	K_2CO_3	90	1.5	93
8	Pd/polymer	1.5	styrene	dioxane	Cs_2CO_3	80	2	93
9	Pd/polymer	0.6	styrene	p-xylene	NBu_3	100	6	92
10	Pd/dendrimer	0.1 - 1	tBA	toluene	K_2CO_3	140	4	85
11	Pd/dendrimer	0.3	MA	CH_3CN	NEt_3	82	8	96
12	Pd/chitosan	0.35	BA	NBu_4Br	NBu_4OAc	115	0.08	95
13	Pd/chitosan	0.01	AA[c]	DMF	NEt_3	80	4	93
14	Pd/MCM-41	10^{-4}	BA	NMP	NEt_3	100	96	98
15	Pd/MCM-41	0.003	MA	DMF	NEt_3	70	4	92
16	Pd/MCM-NH_2	0.3	AA	DMF	NEt_3	70	2	94
17	Pd/Al-MCM-41	5	BA	[bmim]PF_6	NaOAc	130	20	26
18	Pd/ETS-10	$5*10^{-4}$	EA[d]	DMF	NBu_3	130	1	96
19	Pd/LDH	0.4	styrene	DMF	NBu_3	120	16	98
20	Pd/mordenite	0.125	BA	toluene	NBu_3	130	2	92
21	Pd/HY or Beta	0.3	MA	o-xylene	K_2CO_3	153	2.5	100
22	Pd/silica	0.03	BA	NMP	Na_2CO_3	140	6	99
23	Pd/C	0.05	EA	A336	NEt_3	100	0.3	100

a) butyl acrylate
b) methyl acrylate
c) acrylic acid
d) ethyl acrylate

Table 2: Selected heterogeneously catalyzed Heck reactions of 4-bromoacetophenone [29].

Entry	Catalyst	Cat. Conc. [mol%]	Alkene	Solvent	Base	T [°C]	t [h]	Yield [%]
1	Pd nanoparticles	0.1	BA	DMA	NaOAc	120	1	89
2	Pd/MCM-41	10^{-4}	BA	NMP	NEt_3	170	16	98
3	Pd/hydroxyapatite	0.002	styrene	NMP	K_2CO_3	130	20	96
4	Pd/mordenite	0.125	BA	toluene	NBu_3/ NBu_4Br	130	144	76
5	Pd/Al_2O_3	0.1	BA	DMAc	NaOAc	120	3	97
6	Pd/C	0.05	EA	isooctane/ A336	NEt_3	100	20	80

Kinetic experiments showed that monomeric Pd complexes (like $[Pd(NH_3)_4]_2$) on zeolites have reaction rates by orders of magnitude higher than Pd particles. Complete conversion with 0.45 mol% Pd in the Heck reaction of iodobenzene and styrenewas achieved after 16 hours. The coupling of activated aryl bromides was much slower (20 – 28 hours). By usingbutyl acrylate or 4-bromo-substituted styrene, the reaction is complete after 4 – 7 hours. $[PdCl_2(PhCN)_2]$ on silica gel could be reused several times in the reaction of iodobenzene and styrene [8]. Reactions with $Pd(OAc)_2$ or $PdCl_2$ under similar conditions showed that $Pd(OAc)_2$ is as active as the supported

catalyst, whereas $PdCl_2$ yields only 7 % conversion [9,10]. Iodobenzene is converted faster but the reaction was not complete after 12 hours [11]. A complete conversion of iodobenzene was done with 0.05 mol% Pd (2 hours, 80 °C) [12]. The Ni, Cu and Co/SiO_2 catalysts showed high activity for aryl iodides and acrylic acid or styrene. Perosa and coworkers reported complete conversion in the coupling of iodobenzene and ethyl acrylate (4 hours) without any solvent. With iodobenzene and less activated alkenes, compared to butyl acrylate, the yields were worse. Reetz and de Vries used ligand free Pd(OAc)2 (0.02 mol%) in the reaction of bromobenzene and butyl acrylate. It allows almost complete conversion of bromobenzene. Many different approaches have been still made to have homogeneous Pd complexes using different ligands like substituted phosphines or carbenes. Apart from homogeneous catalysts, a number of heterogeneous catalyst systems have been developed for the conversion of bromobenzene. Rotello and coworkers reported about stabilization of Pd nanoparticles by "Mixed Monolayer Protected Clusters" (MMPCs) and achieved 30 % conversion of bromobenzene with styrene(2 hours) [13]. 0.5 mol% Pd(dba)2 was used for the reaction of bromo-benzene and butyl acrylate (84 % yield, 16 h). Lin and Luo worked on a soluble polystyrene-supported palladacycle for the Heck reaction of bromobenzene and methyl acrylate. Catalyst concentration of 5 mol% was necessary for 97 % yield at 130 °C (48 h) [14]. Mesoporous Materials and Zeolites Mesoporous materials and zeolites are also very important for the preparation of solid Pd catalysts. It showed high TON (153,000) in the reaction of bromobenzene and butyl acrylate (72 % conversion). Very long reaction time and high temperature (170 °C) had to be applied [15]. Investigations on Pd catalysts shows that on different zeolites (Na- and H-Mordenite, HY) [16] did not show variations of catalytic activity for different supports. Using PdCl2/KX gave 97 % yield of trans-stilbene (72 hours reaction time) in o-xylene, also 1:1- mixture of trans-stilbene and 1,1-diphenylethylene was found after 48 hours if exchanged CsX was applied [17]. They describe the controlled synthesis of hydroxyapatite-supported Pd complexes and their application in Heck reactions of bromobenzene with styrene and butyl acrylate [18]. For both, high TON (up to 47,000) were reachedwith low catalyst concentrations (2*10-3 mol%) (120 °C,24 hours).Later reportsshowed that different Pd dispersion, reduction degree and leaching tendency are responsible for the small differences in activity. Carbon Solid Pd/C catalysts is part of another important group of heterogeneous catalysts. Researchers have tried to overcome this problem of low activity of Pd/C catalysts by using ionic liquids. Studies on the influence of the preparation

method in highly active catalysts that achieved 90 % conversion within 2 hours if only 0.0025 mol% Pd were applied (TON = 36,000; TOF = 18,000 h-1) [19].In 1997, Ying and coworkers presented Pd-grafted mesoporous materials as catalysts. Pd-TMS11 catalyst was one of the very first heterogeneous catalysts that succeeded in the activation of aryl chlorides (170 °C and 32 hours reaction time). Although a high E:Z ratio of stilbenes (99:1) was obtained, only 40 % selectivity to the Heck coupling products (= 6 % yield) could be achieved [20,21]. Pd modified zeolite NaY was used as a heterogeneous catalyst for reactions of 4-choroacetophenone [22,23], the [Pd(NH3)4]2 showed a much higher activity in the reaction of 4-bromofluoro-benzene and styrene than Pd(OAc)2 and [Pd(C3H5)Cl]2. Addition of NBu4Br had a promoting effect on the reaction(the yield could be increased from 45 to 60% (20 h)). Non- and deactivated aryl chlorides could be converted under optimized reaction conditions by changing solvent (NMP instead of DMA), base (Ca(OH)2 instead of NaOAc) and atmosphere (O2 instead of argon).Sasson and coworkers did convert several non-and deactivated aryl chlorides using 0.7 mol% Pd/C catalyst (100 °C) within 5.5 hours [24]but with from low selectivity (only 0 to 60 % selectivity). Aryl chlorides could be converted by 3 mol% Pd almost quantitatively within one hour with heating. For non-activated aryl The conversion can happen under the same conditions using dioxane and Cs2CO3 as base and solvent, no special conditions like addition of NBu4Br are needed but no differences in activity of aryl iodides, bromides and chlorides wereobserved.

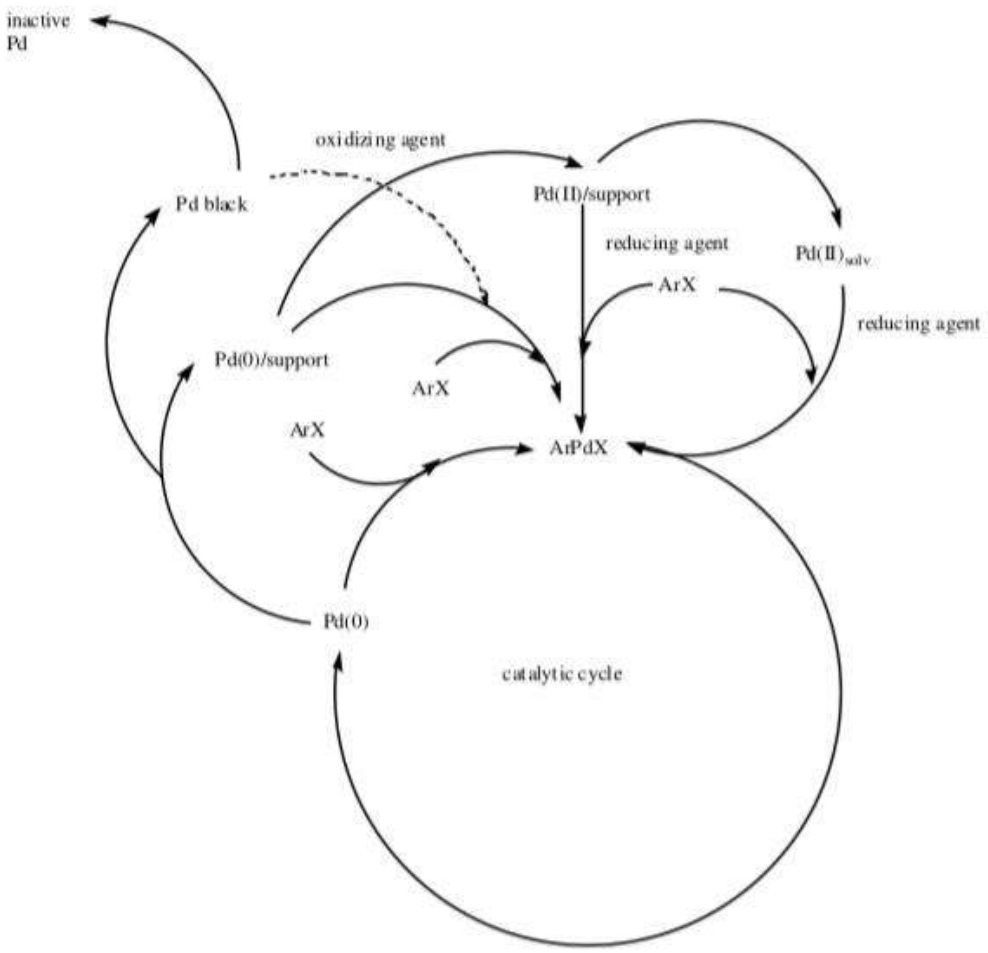

Fig 1: Possible Reaction Pathways, Processes and Pd species Occurring During The Heck Reaction [ref]

Several experiments indicate that the oxidative addition of the arylhalide to a surface Pd(0) atom introduces the actual dissolution step for aryl bromides (and activated aryl chlorides) in the absence of additional ligands (NBu4Br) [25,26]. The sequence of oxidative addition and Pd dissolution can be different in the presence of additional ligands like bromide ions (NBu4Br); possibly Pd dissolution is initiated by complex formation with the halide in this case [27]. Before oxidative addition of the aryl halide is possible, the metal (ions) must be present as (reduced to) Pd(0). The best heterogeneous palladium catalysts contain, however, Pd(II) oxide particles on the support surface (or alternatively Pd(II) complexes in zeolite cages) intheir initial state. For aryl bromides, these systems mainly represent true ligand free catalysts. For aryl chlorides, additional halide ligands (mainly Br-) are used to achieve a comparable situation. Possible reaction

pathways, processes and Pd species occurring during the heck reaction are summarized in the above figure.

➢ CONCLUSION:

Pd catalysed reactions especially Heck reactions are highly useful for organic synthesis, fine chemical production and industrial applications. In the last decade, a number of reports showed the potential of Heck reactions. Pd supported on carbon, on oxides, on/in zeolites, on mesoporous materials, on polymers even Pd colloid systems did activate aryl iodides and chosen aryl bromides. New successful approaches and strategies led to the activation of deactivated aryl bromides and at times, also of aryl chlorides by heterogeneous catalysts. But in the midst of this progress,we still face numerous challenges everyday related to this reaction.So, there is always room for new perspectives and approaches.It is believed that the activation of aryl bromides and aryl chlorides by heterogeneous catalysts will open new interesting applications in the next years as there is still a large scope in future to know and study & research further about Heck Reactions.

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